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Infrared Absorption Spectra in the Study of Mutarotational Equilibria of Monosaccharides

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The infrared absorption spectra (in the range of 5000 to 250 cm^{-1}) of 6 anomeric pairs of sugars and of 12 single anomers are presented, together with the spectra (in the range of 5000 to 667 cm^{-1}) of the dry lyophilizates of the respective equilibrium solutions of these 18 sugars in water.

Analysis of the spectra indicated the presence, in a number (possibly, in all) of the equilibrium mixtures, of some of the carbonyl form (aldehydo or keto) of the respective sugar. Conclusions as to the other components of each equilibrium mixture agreed with those derived from mutarotational studies, except for D-lyxose and D-ribose. Despite the reported absence of mutarotation for D-*gluco*-heptulose and D-*manno*-heptulose, the equilibrium mixture of each was found to contain one or more forms different from that originally dissolved.

1. Purpose and Scope of the Project

This project was primarily undertaken with the objective of gaining, for a number of monosaccharides, information regarding the composition of the sugar mixture obtained by dissolving one anomer of a sugar in water and allowing the solution to reach mutarotational equilibrium. Each such solution was freed from water by lyophilization; and the infrared absorption spectrum of the product was recorded and then compared with the spectrum of the crystalline anomer originally dissolved (and with that of the other anomer, if available).

The second objective was to record these spectra for use in (a) the identification of monosaccharides and (b) eventual assignment of conformation to each crystalline anomer. For 6 sugars, the infrared spectrum, in the range of 5000 to 667 cm^{-1}, was recorded for *both* crystalline anomers and for the equilibrium mixture. For 12 other sugars, only *one* crystalline anomer was available; its infrared spectrum and that of the corresponding equilibrium mixture were recorded in the above range. The infrared spectra in the range of 667 to 250 cm^{-1} were also recorded for the crystalline anomers.

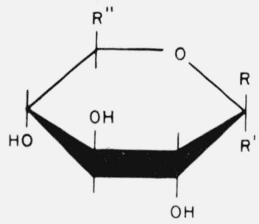
2. Sugars Investigated

Table 1 gives a list of the sugars, their code numbers [1],[1] and an index to the spectrograms; the serial number of a sugar is the same as the number of its spectrogram, and the letter E is appended to designate an equilibrium mixture. The 24 anomers were classified into 4 groups; the members of each group have like configurational features.

[1] Figures in brackets indicate the literature references at the end of this paper. The references for tables 1 and 2 are given at the ends of the tables.

2.1. Sugars of the *xylo* Configuration

The members of this group have the general formula I, if they are pyranoid.

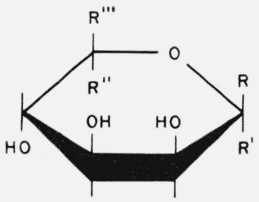


I

1. α-D-Xylose, R=H; R′=OH; and R″=H.
2. (?)-L-*xylo*-Hexulose (L-sorbose), R=OH and R′=CH_2OH, or vice versa; R″=H; and the molecule is the mirror image of that depicted.
5. α-D-Glucose, R=H; R′=OH; and R″=CH_2OH.
6. β-D-Glucose, R=OH; R′=H; and R″=CH_2OH.
7. α(?)-D-*gluco*-Heptulose, R=CH_2OH; R′=OH; and R″=CH_2OH.

2.2. Sugars of the *lyxo* Configuration

These sugars, if pyranoid, have the general formula II.



II

8. α-D-Lyxose, R=H; R′=OH; and R″ and R‴ =H.

9. β-D-Lyxose, R=OH; and R′, R″, and R‴=H.

10. (?)-D-*lyxo*-Hexulose (D-tagatose), R=CH_2OH and R′=OH, or vice versa; and R″ and R‴ =H.

11. 6-Deoxy-α-L-mannose (α-L-rhamnose) monohydrate, R=H; R′=OH; R″=H; R‴=CH_3; and the molecule is the mirror image of that depicted.

12. 6-Deoxy-β-L-mannose (β-L-rhamnose), R=OH; R′=H; R″=H; R‴=CH_3; and the molecule is the mirror image of that depicted.

13. α-D-Mannose, R=H; R′=OH; R″=H; and R‴ =CH_2OH.

14. β-D-Mannose, R=OH; R′=H; R″=H; and R‴ =CH_2OH.

TABLE 1. *Compounds measured and index to spectrograms*

Code	Sugar	References	Spectrogram
10.11?0	α-D-Xylose	1, 2	1
10.1100	D-Xylose (equilibrium)		1–E
10.71?0	(?)-L-*xylo*-Hexulose [a]	3, 4	2
10.7100	L-*xylo*-Hexulose (equilibrium)		2–E
10.21?09899	α-D-Glucose·0.5 NaCl·0.5 H_2O	5	3
10.21?099	α-D-Glucose, monohydrate	6, 7	4
10.2110 [b]	α-D-Glucose	2, 6 to 9	5
10.2100[99]	D-Glucose (equilibrium)		5, 6–E
10.21?0	β-D-Glucose	2, 7, 10	6
10.81?0	α(?)-D-*gluco*-Heptulose	11	7
10.8100	D-*gluco*-Heptulose (equilibrium)		7–E
10.12?0	α-D-Lyxose	2, 12 to 14	8
10.1200	D-Lyxose (equilibrium)		8, 9–E
10.12?0	β-D-Lyxose	2, 14	9
10.72?0	(?)-D-*lyxo*-Hexulose [c]	15	10
10.7200	D-*lyxo*-Hexulose (equilibrium)		10–E
10.22?0(6)8099	6-Deoxy-α-L-mannose, monohydrate [d]	2, 16	11
10.2200(6)8099	6-Deoxy-L-mannose (equilibrium)		11, 12–E
10.22?0(6)80	6-Deoxy-β-L-mannose	17 to 19	12
10.22?0	α-D-Mannose	2, 20	13
10.2200	D-Mannose (equilibrium)		13, 14–E
10.22?0	β-D-Mannose	2, 21	14
10.82?0	(?)-D-*manno*-Heptulose	22	15
10.8200	D-*manno*-Heptulose (equilibrium)		15–E
10.26?09899	(?)-D-Gulose·0.5 $CaCl_2$·0.5 H_2O	2	16
10.26009899	D-Gulose·0.5 $CaCl_2$ (equilibrium)		16–E
10.13?0	β-D-Arabinose	23	17
10.1300	D-Arabinose (equilibrium)		17–E
10.73?09899	(?)-D-*arabino*-Hexulose [e]·0.5 $CaCl_2$·1.5 H_2O.	24	18
10.73009899	D-*arabino*-Hexulose·0.5 $CaCl_2$ (equilibrium).		18–E
10.73?0(3)11	3-*O*-Methyl-(?)-D-*arabino*-hexulose	25	19
10.7300(3)11	3-*O*-Methyl-D-*arabino*-hexulose (equilibrium).		19–E
10.82?0(3)7699	β-D-*manno*-3-Heptulose, monohydrate.[f]	26	20
10.8200(3)7699	D-*manno*-3-Heptulose (equilibrium)[f]		20–E
10.23?0(6)80	6-Deoxy-α-L-galactose [g]	27 to 30	21
10.2300(6)80	6-Deoxy-L-galactose (equilibrium)		21–E
10.23?0	α-D-Galactose	2, 31 to 34	22
10.2300	D-Galactose (equilibrium)		22, 23–E
10.23?0	β-D-Galactose	2, 31 to 34	23
10.87?6899	2,7-Anhydro-β-D-*altro*-heptulose,[h] monohydrate.	35	24
10.8700+ 10.87?6899, etc.[j]	Mixture from acid treatment of compound 24 (equilibrium) [j]		24–E
10.14?0	β(?)-D-Ribose	36, 37	25
10.1400	D-Ribose (equilibrium)		25–E
10.24?0	α-D-Talose	2, 38, 39	26
10.2400	D-Talose (equilibrium)		26, 27–E
10.24?0	β-D-Talose	39	27

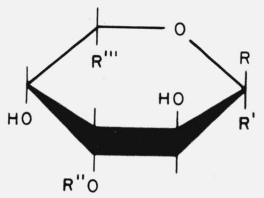
[a] Trivial name: L-sorbose. [b] α-D-Glucopyranose has the CA conformation [T. R. R. McDonald and C. A. Beevers, Acta Cryst. **5**, 654 (1952)]. [c] Trivial name: D-tagatose. [d] Trivial name: α-L-rhamnose monohydrate. [e] Trivial name: D-fructose. [f] Kindly presented by R. Schaffer. [g] Trivial name: α-L-fucose. [h] Trivial name: sedoheptulosan. [j] See text, sec. 6.2.

15. (?)-D-*manno*-Heptulose, R=CH_2OH and R′ =OH, or vice versa; R″=H; and R‴ =CH_2OH.

16. (?)-D-Gulose ·0.5 $CaCl_2$ ·0.5 H_2O, R=H and R′ =OH, or vice versa; R″=CH_2OH; R‴=H; and the molecule is the mirror image of that depicted.

2.3. Sugars of the *arabino* Configuration

These sugars, if pyranoid, have the general formula III.



III

17. β-D-Arabinose, R=OH; R′=H; and R″ and R‴ =H.

18. (?)-D-*arabino*-Hexulose (D-fructose)· 0.5 $CaCl_2$ ·1.5 H_2O, R=OH and R′=CH_2OH, or vice versa; and R″ and R‴=H.

19. 3-*O*-Methyl-(?)-D-*arabino*-hexulose, R=OH and R′=CH_2OH, or vice versa; R″=CH_3; and R‴=H.

20. β-D-*manno*-3-Heptulose monohydrate, R=OH; $R'=HOH_2C-\underset{OH}{\overset{H}{C}}$; and R″ and R‴=H.

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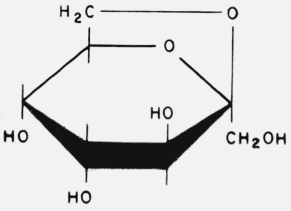
21. 6-Deoxy-α-L-galactose (α-L-fucose), R=OH; R′=H; R″=H; and R‴=CH_3.

22. α-D-Galactose, R=OH; R′=H; R″=H; R‴=CH_2OH; and the molecule is the mirror image of that depicted.

23. β-D-Galactose, R=H, R′=OH; R″=H; R‴=CH_2OH; and the molecule is the mirror image of that depicted.

Compound 24 (sedoheptulosan) has the following formula (IV).

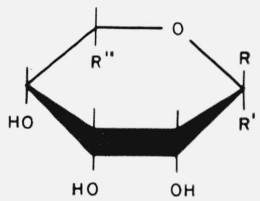


IV

24. 2,7-Anhydro-β-D-*altro*-heptulopyranose

2.4. Sugars of the *ribo* Configuration

The pyranoid forms of these sugars have the general formula V.



V

25. β-D-Ribose, R=OH; R′=H; and R″=H.

26. α-D-Talose, R=OH, R′=H; R″=CH_2OH; and the molecule is the mirror image of that depicted.

27. β-D-Talose, R=H, R′=OH; R″=CH_2OH; and the molecule is the mirror image of that depicted.

3. Previous Infrared Studies of These Sugars

3.1. Spectra Recorded for the Solid Phase

In 1950, Kuhn [2] recorded the spectra of 10 of the crystalline sugars, each in Nujol suspension, but, except for α-D-glucose (compound 5), he did not mention which anomer was employed. Sugars for which *only one* anomer is normally available were, presumably, sugars 1, 2, 21, 25, and the epimer of 17. The other five might have been 4 or 5, 5 or 6, 11 or 12, 13 or 14, and 22 or 23; by comparison of our spectrograms with his, we can now identify the anomers he employed as 4, 5, 11, 14, and 22. For sugars 5 and 14, the spectra were recorded for the range of 5000 to 667 cm^{-1}; for the 8 other sugars, from 1250 to 667 cm^{-1}. For sugar 14, Kuhn also recorded the spectrum of a film of the sugar, obtained by evaporation of an aqueous solution, which was probably either partially or completely equilibrated.

Four years later, the spectrum of sugar 5 ("α-glucose"; enantiomer not stated) as a mull in hexachlorobutadiene was recorded [3] for the range of approximately 3500 to 3200 cm^{-1}. In addition, Barker and coworkers [4] discussed bands in the range of 973 to 670 cm^{-1} shown by the spectra of the following 9 sugars in Nujol suspension: 1, 5, 6, 11, 14, 17, 21(?), 22, and 23. However, the spectra were published in insufficient detail to permit comparison with ours over a wide spectral range. Similarly, in 1957, Konkin and coworkers [5] published the spectra in the range of 3600 to 2700 cm^{-1} for a mull of each of the following sugars (anomer and suspension medium not specified): 1, 5 or 6, 13 or 14, enantiomer of 17, D-fructose, and 22 or 23. In the same year, Farmer [6] published the spectrum of sugar 5 ("α-glucose"; enantiomer not specified) in a potassium bromide pellet for the range of 5000 to 625 cm^{-1}. Finally, in 1959, Urbański and coworkers [7] recorded spectra and tabulated bands for 6 of these sugars in Nujol mulls for the range of 4000 to 750 cm^{-1}, but did not mention which anomer (of each) they employed. By comparison of our spectrograms with theirs, we have identified these sugar anomers as 1, 2, 5, 14, enantiomer of 17, and 25. [However, the equilibrium rotation that they recorded for D-ribose (sugar 25) is actually that for L-ribose, and their melting point for the D-glucose anomer they examined is closer to that for the β anomer (sugar 6) than for the α anomer (5).]

3.2. Spectra Recorded for the Liquid Phase

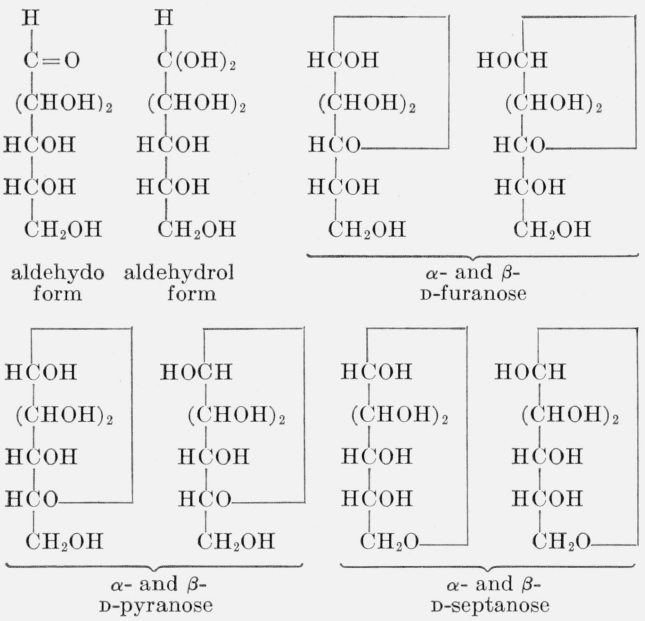
Long ago, Coblentz [8] recorded the infrared spectra of D-fructose and D-glucose monohydrate (sugar 4), presumably as supercooled melts, in the range of 10,000 to 1333 cm^{-1}. Rogers and Williams [9] listed absorption bands (3030 to 960 cm^{-1}) for equilibrated, saturated, aqueous solutions of L-xylose (enantiomer of 1–E), D-glucose (5,6–E), D-lyxose (8,9–E), D-mannose (13,14–E), D-arabinose (17–E), D-galactose (22,23–E), and D-fructose. Next, Barr and Chrisman [10] recorded the infrared spectrum (5556 to 3846 cm^{-1}) of a saturated, aqueous solution of D-arabinose (17–E). For other sugars, they smeared a concentrated aqueous solution of the sugar on a cover glass and heated gently for several hours, obtaining a thick sirup which, they claimed, contained practically no water; after this treatment, each sugar was probably present as its equilibrium mixture. The spectra of these evaporated films (for the range 5556 to 2174 cm^{-1}) were recorded for D-xylose (1–E), D-glucose (5,6–E), L-rhamnose (11,12–E), D-mannose (13,14–E), L-arabinose (enantiomer of 17–E), D-galactose (22,23–E), and D-fructose.

Finally, Parker [11] recorded the spectra (for the range of 1667 to 909 cm^{-1}) of 20-percent aqueous solutions (w/v) of L-arabinose (enantiomer of 17–E), D-ribose (25–E), and D-fructose, and of a 10-percent aqueous solution of D-galactose (22,23–E). In addition, he recorded the spectra (for the same range) of 20-percent aqueous solutions of α-D-glucose, β-D-glucose, and β-D-mannose (a) 2.5 minutes

after dissolution, and (b) at the end of mutarotation. By following the change in percent transmittance (at 1143 cm^{-1} for α- or β-D-glucose, and at 1163 cm^{-1} for β-D-mannose) with time, he was able to determine the mutarotation constants; these agreed well with those determined from measurements of change in optical rotation (see sec.4).

4. Mutarotational Studies of These Sugars by Optical Rotation

When a crystalline sugar is dissolved in water and the solution is allowed to stand, the optical rotation initially observed may change. An aldohexose or a 2-heptulose, in solution, may adopt one or more of eight modifications. Thus, for an aldohexose in which C–4 and C–5 are both D, the following structures may theoretically be present in the equilibrium solution. Of these, only the aldehydo form will show carbonyl absorption in the infrared spectrum.



For an aldopentose or a 2-hexulose, the septanose forms are impossible, so that, for them, the maximum number of theoretically possible sugar components is six.

It is, of course, possible that the appearance of new species in the solution may be unaccompanied by any change in optical rotation. This would occur if (a) all the species present at any moment have the same optical rotation; (b) the initial and final rotations are the same, but, although intermediate rotations are different, mutarotation is so rapid that it is complete before observation of optical rotation has been started; or (c) an increase in rotation, caused by appearance (or disappearance) of one or more forms, is exactly balanced by a decrease resulting from disappearance (or appearance) of one or more other forms. In addition, there is the possibility that, at all times during establishment of equilibrium, the changes in rotation are so slight as to be virtually unobservable. On the other hand, in some instances, an apparent or spurious mutarotation, caused by a positive or negative heat of solution, might be observed, even though no new species actually appeared in the solution.

When dynamic equilibrium between the forms is reached, the proportion of each that is present in the solution depends on the structural, configurational, and conformational stability of each form.[2] Some indications as to the proportions of the various forms present in the equilibrium solution of some of the sugars in the present study have been obtained by observing the change in optical rotation, with time, when a crystalline anomer of the sugar is dissolved in pure water. The results [2] are given in table 2, from which it may be seen that, as regards mutarotational behavior, 4 groups of sugars may be distinguished.

In *group 1*, exhibiting little or no mutarotation, are the 2-ketoses 2, 7, 10, and 15; the equilibrium mixture for each of these sugars appears to consist almost entirely of one form (possibly the α- or β-pyranose), which may be the same as the crystalline sugar dissolved.

Group 2 sugars (the 2-ketoses 18 and 19, and, perhaps, the 3-ketose 20) exhibit mutarotation, and the equilibrium mixture apparently consists mainly of a single pyranose form together with the α- and β-furanose forms.

[2] A discussion, prepared by H. S. Isbell, of the sugars in solution is given in F. J. Bates and Associates, NBS Circular **440,** Chapter XXIX (1942).

TABLE 2. *Character of the mutarotation and composition of the equilibrium mixture, as determined by studies of changes of optical rotation*

Sugar		Mutarotation reaction	Equilibrium mixture	Reference
Name	No.			
(?)-L-*xylo*-Hexulose	2	slight; complex	almost entirely one form (pyranose) that is the same as for the crystals	1
α(?)-D-*gluco*-Heptulose	7	none	?-	2
(?)-D-*lyxo*-Hexulose	10	none	almost entirely one form (pyranose)	3
(?)-D-*manno*-Heptulose	15	none	?-	4
(?)-D-*arabino*-Hexulose ·0.5 $CaCl_2$·1.5H_2O	18	mutarotates	a single pyranose +α- and β-furanoses	5
3-*O*-Methyl-(?)-D-*arabino*-hexulose	19	mutarotates	?-	6
β-D-*manno*-3-Heptulose	20	mutarotates	?-	7
α-D-Xylose	1	first order	mainly α-pyranose+ β-pyranose	8
D-Glucose, α-;β-	5; 6	first order		8
D-Lyxose, α-;β-	8; 9	first order		8
6-Deoxy-L-mannose, α-;β-	11; 12	first order		8
D-Mannose, α-;β-	13; 14	first order		8
(?)-D-Gulose ·0.5 $CaCl_2$· 0.5 H_2O	16	first order		8
β-D-Arabinose	17	complex	α-pyranose+ β-pyranose+ α-furanose+ β-furanose	8
6-Deoxy-α-L-galactose	21	mutarotates		9
D-Galactose, α-;β-	22; 23	complex		8
β(?)-D-Ribose	25	complex		8
D-Talose, α-;β-	26; 27	complex		8,10

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For *group 3* (aldoses 1, 5 and 6, 8 and 9, 11 and 12, 13 and 14, and 16), the mutarotation is a first-order reaction, and the equilibrium mixture consists mainly of the α- and β-pyranose forms.

The members of *group 4* (aldoses 17, 21, 22 and 23, 25, and 26 and 27) exhibit a complex mutarotation, and the equilibrium mixture appears to contain, at least, the α- and β-pyranose forms and the α- and β-furanose forms.

5. Discussion of the Spectra

5.1. Spectra of Sugars for Which Both Anomers Were Available

For D-glucose, D-lyxose, L-rhamnose, D-mannose, D-galactose, and D-talose, the infrared spectra were recorded for both of the crystalline anomers. Table 3 lists the bands shown by the α anomer but not by the β anomer of each of these sugars, and table 4 lists the bands shown by the β anomer but not by the α anomer of each. These bands will be discussed in a subsequent article dealing with the infrared spectra of pyranoid sugars.

5.2. Spectra of the Equilibrium Mixtures

In this discussion, the spectrum of the material obtained by lyophilizing the equilibrium solution of a sugar will be referred to as the "equilibrium spectrum" for that sugar. It was assumed that, during freezing and lyophilization, no change in composition of an equilibrium solution occurs; for some sugars, this assumption may be unwarranted, and crystallization of a new form, or of the original form, may take place.

The equilibrium spectra all showed a band near 1718 cm^{-1}, suggesting the presence, in every equilibrium mixture, of some of the carbonyl form (aldehydo or keto) of the respective sugar. The intensity of this band differed from sugar to sugar; for example, for D-mannose (13,14–E) and D-galactose (21,22–E), it was quite clearly present, whereas it was weaker for D-fructose (18–E) and D-glucose (5,6–E), and barely perceptible for some of the other sugars. This observation agrees with the results of Lippich [12], who found that the proportion of the carbonyl form present in the equilibrium solution is in the order D-mannose>D-galactose>D-fructose>D-glucose. Similarly, D-*manno*-2-heptulose (15–E), whose aqueous solution shows [13] an ultraviolet absorption maximum at 2650A, indicating the presence of the carbonyl form, exhibits an infrared absorption band at 1712 cm^{-1}. D-*manno*-3-Heptulose, which is a member of the D-*arabino* series, shows a much stronger carbonyl band (at 1727 cm^{-1}).

The equilibrium spectra of those sugars for which the spectra for *both* crystalline anomers were available were now studied. These equilibrium spectra were found to fall into 2 groups. In the *first group*

TABLE 3. *Bands (cm^{-1}) shown by the α anomer but not by the β anomer of six sugars.*

D-Glucose (5)	D-Lyxose (8)	L-Rhamnose·H_2O (11)	D-Mannose (13)	D-Galactose (22)	D-Talose (26)
[a]3413	----	----	----	----	3378
----	----	3247	3165	3195	----
3021	----	2950	2976	----	----
2899	----	2899	2924	2890	2865
----	----	2584	----	2532	2674
----	----	1669	----	----	----
1445	1437	----	1453	1447	----
1429	----	1429	----	----	1425
[a]1340	----	----	1385	----	1362
1297	----	----	1297	1328, 1314	----
1284	1285	----	----	1284	----
----	1244, 1220	----	1224	1250	----
----	1147	----	1199	1152	1144
1105	----	----	1104	1104	----
1050	----	1075	----	1070, 1046	1054
[a]996	----	----	972	997, 976	----
----	965	----	960	[b]958	952
----	----	----	915	----	908
----	867	[b]878	885	----	----
[a b]838	852	[b]830	831	----	----
----	----	----	812, 804	----	802
[a b]776	771	----	----	[b]766	----
----	----	----	707	----	715
----	----	658	679	660	676
621	627	----	----	----	----
----	583	570	565	----	----
557	549, 530	----	----	533	----
----	490	503	509	500	----
435	476	----	467	----	477
391	----	----	391	----	----
377	367	----	375	----	366
347	----	----	----	345	----
----	----	----	311	334, 329	----
----	294	301	----	300(?), 292	296
----	----	----	----	280	----

[a] These bands were mentioned by Urbański and co-workers [7].
[b] These bands were mentioned by Barker and co-workers [4].

TABLE 4. *Bands (cm^{-1}) shown by the β anomer but not by the α anomer of six sugars.*

D-Glucose (6)	D-Lyxose (9)	L-Rhamnose (12)	D-Mannose (14)	D-Galactose (23)	D-Talose (27)
----	----	----	----	----	3497
----	----	----	----	----	3436
3247	3257	----	----	3333	3247
----	----	----	----	----	3030
----	----	2915	----	----	2924
----	----	2874	2874	2857	2890
----	----	2747	----	----	2703
----	1473	----	1484	----	1511
----	1420	----	1433	1435	1439
1361	1374	----	1410	----	1393
----	----	----	----	----	1340
1311	1318	----	[b]1311	----	1290
1271, 1253	----	1259	----	1269	1248
----	----	----	----	1212	----
----	1163	1166	[b]1170	1166	1176
----	----	1131	----	1120	----
----	1092	1100	1089	1089	1074
1063	----	1052	----	----	----
----	----	----	----	1033	1032
----	----	1025	----	1019	----
----	----	----	[a b]936	[a]945	935
[a]901	----	897	[a b]899	[a]900	886
----	804	865	[a b]862	----	879
----	----	777	[a b]772	----	----
----	755	----	729	----	746
709	----	672	----	654	653
----	615	----	619	----	----
----	----	530	540	553(?)	548
519	513	----	----	----	495
460	464	----	----	----	----
----	446	----	448	----	----
----	416	421	426	----	----
----	----	325	285	----	----

[a] See footnote b to table 3.
[b] See footnote a to table 3.

TABLE 5. *Bands (cm^{-1}) in the infrared spectra of the equilibrium mixtures of four sugars, compared with corresponding bands for each anomer of these sugars.*

D-Glucose			L-Rhamnose			D-Mannose			D-Galactose		
5,6–E	5	6	11,12–E	11	12	13,14–E	13	14	22,23–E	22	23
3356	[a] 3322	3356	3378	3333	—	3378	3344	3367	3367	3390	3413
....	....	....	2985	2985	2976	2941	2976	—	....	....	....
2924	2941, 2899	2941	2933	2950, 2899	2915	2907	2924	—	2941	2941	2950
2717	2688	2747	2717	2703	2695	2747	2703	2688	....	....	....
1712	—	—	1724(?)	—	—	[b] 1724	—	—	[b] 1730	—	—
1647	—	—	1650	1669	—	....	....	....	....	....	....
....	....	....	1456	1449	1449	....	....	....	....	....	....
1420	1429	1412	1418	1429, 1403	1406	1418	1422	1422	1416	1425	1416
[b] 1364	—	1361	1385	1383	1379	1385	1385	1372	[b] 1379	—	1383
1321	—	1311	1330	1330	1342, 1323	[b] 1332	1332	1337	1330	1328	—
1282	1284	1271	....	....	....	....	....	....	....	....	....
1263	—	1253	1258	—	1259	1259	1255	[a] 1263	1256	1250	1269, 1241
1200	[a] 1202	1202	1229	1224	1225	1211	1208	[a] 1214	1220	—	1212
....	....	....	1176	—	1166	[c] 1166	—	[a c] 1170	....	....	....
[c] 1147	[a c] 1148	[c] 1155	1140	1143	1149	....	....	....	1144	1140	1133
[b] 1104	[a] 1111, 1105	1111	1125	1122	1121	1111	1111	[a] 1111	....	....	....
1080	[a] 1080	1082	1087	1086	1089	1082	1073	1089	1078	1081	1080
....	....	....	1066	1070	1052	1068	1067	[a] 1073	....	....	....
....	....	....	....	....	....	1059	—	1062	1046	1046	1054
1035	[a] 1026	1035	1018	—	1025	[b] 1029	1034	1035	....	....	....
[b] 995	[a] 996	—	978	979, [d] 976	979	973	972	—	986	997, 976	—
....	....	....	....	....	....	958	960	—	949	—	[d] 945
921	[a d] 916	[d] 914	....	....	....	934	—	[a d] 936	921	—	—
901	—	[d] 901	904	[d] 911	909	906	—	[a d] 899	894	[d] 890	[d] 900
....	....	....	864	[d] 878	865	870	—	[a d] 862	879	—	[d] 884
840	[a d] 838	—	834	[d] 834	834	829	831	—	....	....	....
....	....	....	808	[d] 805	806	808	812	—	802	[d] 792	—
771	[a d] 776	—	776	—	777	783	—	[a d] 772	786	[d] 792	[d] 781
708	—	709	718	714	718	719	707	729	701	707	700
....	....	....	678	—	672	....	....	....	....	....	....

[a] See footnote a to table 3.
[b] These bands were mentioned by Rogers and Williams [9].
[c] These bands were mentioned by Parker [11].
[d] See footnote b to table 3.

(see table 5), all bands observed in the equilibrium spectrum (excepting that for carbonyl, at about 1718 cm^{-1}) could be accounted for, either as being (a) distinctive of one anomer present (the bands matching those of one or both of the crystalline anomers) or (b) the resultant of overlapping of neighboring bands displayed by each of the two crystalline anomers, respectively. In this category (for which the equilibrium mixtures consist, presumably, of 3 sugar components, viz, the α- and β-pyranose forms and the open-chain form) were the equilibrium spectra of D-glucose (5,6–E), L-rhamnose (11,12–E), D-mannose (13,14–E), and (except for one band, at 921 cm^{-1}) D-galactose (22,23–E). For the *second group* (see table 6), consisting of D-lyxose (8,9–E) and D-talose (26,27–E), the equilibrium spectrum shows bands (besides the carbonyl band) that are *absent* from the spectrum of *either* of the crystalline anomers. These extra bands may be attributable to the presence of (a) the open-chain form, (b) one or both anomers of one or more ring-forms different from that in the crystalline anomers examined, or (c) the presence of different conformations of the sugar. It is possible that D-galactose should be included in the second group.

For the other crystalline sugars in table 1, only *one* anomer of each was available. On comparing

TABLE 6. *Bands (cm^{-1}) in the infrared spectra of the equilibrium mixtures of two sugars, compared with corresponding bands for each anomer of these sugars.*

D-Lyxose			D-Talose		
8,9–E	8	9	26,27–E	26	27
3448	3509	—	....	....	....
3356	3300	3322	3356	3300	3300
3257	—	3257	....	....	....
2933	2941	2933	2933	2950	2950, 2924
2717	2681	2674	....	....	....
1712(?)	—	—	1724	—	—
1464	1464	1460	....	....	....
1418	1397	1420	1416	1425	—
[a] 1344	1346	1344	1328	1323	1325
1258	1253	1256	1244	1238	1241
....	....	....	1167	—	1176
1136	1133	1130	1115	1115	1122
[a] 1106	1099	1107	1092	1085	1089
1075	1072	1075	....	....	....
1044	1047	1045	1048	1054	—
1005	1006	1006	995	—	—
982	—	—	963	—	—
945	—	—	937	—	935
899	—	—	....	....	....
882	887	883	877	874	879
846	852	840	864	—	871
808	809	809	810	816	812
766	771	—	758	765	765, 746
714	—	713	....	....	....
673	669	673	....	....	....

[a] See footnote b to table 5.

the equilibrium spectrum of each sugar with the spectrum of the corresponding crystalline sugar, two groups of spectra were noted. In the *first* group (see table 7) were the equilibrium spectra [3] of L-*xylo*-hexulose (2–E), D-*lyxo*-hexulose (10–E), D-gulose·0·5 $CaCl_2$ (16–E), D-*arabino*-hexulose·0.5 $CaCl_2$ (18–E), 3-*O*-methyl-D-*arabino*-hexulose (19–E), and D-ribose (25–E); in each of these spectra, all bands which could be clearly distinguished were also present in the spectrum of the crystalline anomer originally dissolved (although the equilibrium spectrum lacked the band-definition of some of the bands displayed by the crystalline anomer). Indeed, for L-*xylo*-hexulose, D-*lyxo*-hexulose, and D-ribose, *the equilibrium spectrum is scarcely distinguishable from that of the crystalline sugar.* (In addition, a considerable resemblance between the equilibrium spectra of D-ribose and D-talose is evident, and, in the range of 5000 to 962 cm^{-1}, the spectra are almost superimposable.)

The *second group* of equilibrium spectra (see table 8) consisted of those of D-xylose (1–E), D-*gluco*-heptulose (7–E), D-*manno*-heptulose (15–E), D-arabinose (17–E), D-*manno*-3-heptulose (20–E), and 6-deoxy-L-galactose (21–E). Each of these equilibrium spectra clearly showed some bands not displayed by the anomer originally dissolved. New species of each sugar were obviously present in the respective equilibrium mixture; for sugars 7 and 15 (see table 2), a change in optical rotation during equilibration either (a) does not occur or (b) is so slight that it has not been detected. Since, for these 6 sugars, the spectrum of the other anomer of each was unavailable, no decision as to the source of the new bands could be made.

Thus, as regards the composition of the equilibrium mixture, the conclusions earlier arrived at (from studies of mutarotation) agree (or do not *dis*agree) with those derived from the infrared spectra, *except for* D-lyxose and D-ribose.

A clearcut decision as to agreement between results derived by the two techniques could not be reached for D-*gluco*-heptulose and D-*manno*-heptulose (as a careful search for mutarotation has not been made for these sugars) or for D-gulose, D-*arabino*-hexulose, and 3-*O*-methyl-D-*arabino*-hexulose (as their equilibrium spectra were not sufficiently informative).

[3] The "equilibrium spectrum" of 2,7-anhydro-D-*altro*-heptulose also belonged to this group, but, as this anhydride had received a special treatment (see sec. 6.2), the compound is not included here.

TABLE 7. *Bands (cm^{-1}) in the infrared spectra of the equilibrium mixtures of six sugars, compared with corresponding bands for one anomer of each of these sugars.*

L-*xylo*-Hexulose		D-*lyxo*-Hexulose		D-Gulose·0.5 $CaCl_2$		D-*arabino*-Hexulose·0.5 $CaCl_2$		3-*O*-Methyl-D-*arabino*-hexulose		D-Ribose	
2–E	2	10–E	10	16–E	16	18–E	18	19–E	19	25–E	25
3390	[a] 3413	3401	3534	....	....	3378	3425	3401	3401	....	....
....	....	3333	3322	3331	3333	3333	3268	....	....	3356	[a] 3378
2941	2950	2941	2950	2941	2915	2950	2985, 2933	2950	2941	2933	2933
2907	2907	....	....	....	....	....	....	2865	2857	2890	2899
2688	2778	2703	2674	2732	2681	2717	2681	....	....	2703	2703
1712	—	1718	—	1724(?)	—	1712	—	1712	—	1718	—
....	....	....	....	1650	1667	1647	1656	....	....	....	....
1464	1466	1473	1471	1456	1462	....	....	1458	1451	1458	1456
....	....	1443	1443	....	....	....	....	....	....	....	....
1399	1397	1410	1408	1416	1410	1425	1425	1410	1435, 1397	1416	1414
1366	1366	1383	1379	....	....	....	....	....	....	....	....
1351	1350	1340	1340	....	....	[b] 1355	1368, 1339	1346	1355	1344	1362
1311	[a] 1312	1302	1304	1305	1300	....	....	....	....	....	....
....	....	1277	1272	....	....	....	....	....	....	....	....
1258	[a] 1258	1263	1264	1259	1241	1259	1250	....	....	1250	[a] 1245
....	....	1241	1239	....	....	1242	1238	1244	1241	....	....
1212	1215	....	....	....	....	....	....	....	....	1227	[a] 1220
1193	[a] 1193	1185	1171	....	....	1185	1183	1190	1190	....	....
1151	[a] 1151	1155	1153	1147	1138	1147	1143	....	....	1139	[a] 1130
1125	1126	....	....	....	....	....	....	1119	1126, 1111	1119	[a] 1117
1106	[a] 1109	1100	1101	1099	1103, 1095	[b] 1099	1112, 1091	....	....	....	....
1080	[a] 1081	1071	1073	....	....	1080	1083	1080	1087	1085	1085
1059	1062	1058	1056	1052	1057	1058	1068, 1049	....	....	....	....
1050	[a] 1049	1042	1038	....	....	....	....	....	....	1044	[a] 1041
1032	[a] 1031	....	....	....	....	....	....	....	....	....	....
1016	1014	1024	1021	....	....	....	....	....	....	....	....
994	[a] 992	....	....	....	....	....	....	1000	994	1004	1017
....	....	964	966	980	963	977	984	973	970	966	[a] 959
....	....	947	947	....	....	....	....	931	928	....	....
....	....	912	912	917	919	929	920	....	....	914	[a] 912
900	[a] 901	....	....	895	897	....	....	....	....	887	[a] 889
885	[a] 882	870	868	883	876	863	860	870	865	870	[a] 869
821	[a] 820	822	822	....	....	822	823	825	831	826	825
....	....	785	784	807	806	783	785	770	768	797	[a] 799
....	....	....	....	....	....	....	....	....	....	747	747
721	719	730	731	....	....	....	....	....	....	724	724
685	683	690	688	....	....	....	....	....	....	....	....

[a] See footnote a to table 3. [b] See footnote b to table 5.

TABLE 8. *Bands (cm^{-1}) in the infrared spectra of the equilibrium mixtures of six sugars, compared with corresponding bands for one anomer of each of these sugars.*

D-Xylose		D-*gluco*-Heptulose		D-*manno*-2-Heptulose		D-Arabinose		D-*manno*-3-Heptulose · H_2O		6-Deoxy-L-galactose	
1-E	1	7-E	7	15-E	15	17-E	17	20-E	20	21-E	21
3356	[b] 3333	3356	3413	3356	3401	3356	[b] 3356	3390	3401	3356	3344
....	....	....	....	....	....	....	....	2976	2950	2985	3021
....	....	2933	2959	2941	2933	2924	2959	....	....	....	....
2915	2899	2907	2907	....	....	....	....	....	....	2915	2899
2703	2732	2688	2703	2674	2695	2688	2674	....	....	2717	2732
1712(?)	—	1712(?)	—	1712	—	[a] 1718	—	1727	—	1718	—
1466	1464	....	....	....	....	....	....	1653	1653	1464	—
....	....	....	....	....	....	....	....	1420	1429	1441	1447
1418	1395	1420	—	1412	1404	1406	1404	....	....	1385	1391
[a] 1355	1357	1364	1361	....	....	1346	1357	1359	—	1370	1370
....	....	....	....	....	....	....	....	....	....	1312	1300
1269	—	1255	1263	1250	1264	1258	[b] 1259	1271	—	1247	1256
1244	[b] 1236	....	....	....	....	[a] 1218	[b] 1233	1247	—	1214	1221
1202	1202	1206	1198	1202	1199	....	....	....	....	....	....
....	....	1181	1186	....	....	1161	—	1181	1185	1168	1170
1145	[b] 1149	1111	1117	....	....	1139	[b] 1135	....	....	1126	1130
[a] 1088	[b] 1082	1083	1087, 1078	1096	1093	1096	[b] 1093	1100	1099	1095	1089
....	....	....	....	....	....	[a] 1085	—	1086	—	....	....
1057	1055	1059	1054	1057	1056	1062	1067	....	....	1068	1072
1048	[b] 1042	1040	—	....	....	1033	[b] 1055	1052	1050	1037	1041
1016	1018	1019	1013	1025	1021	....	....	....	....	....	....
979	989	989	986	....	....	1001	[b] 1001	996	—	998	999
....	....	960	—	950	952	....	....	952	—	965	[c] 963
936	[b] 935	....	....	....	....	947	[b] 945	915	918	949	—
898	[b] 904	907	—	903	906	917	—	902	895	900	—
....	....	879	871	....	....	888	[b] 894	....	....	....	....
....	....	....	....	....	....	869	—	....	....	858	—
....	....	832	827	840	—	844	[b] 844	824	818	....	....
812	—	....	....	822	816	....	....	....	....	814	[c] 819
....	....	....	....	....	....	786	[b] 786	789	783	770	[c] 772
759	[b] 762	....	....	744	—	....	....	....	....	758	—
....	....	716	714	704	702	....	....	....	....	....	....
655	—	....	....	....	....	....	....	....	....	667	666

[a] See footnote b to table 5. These authors studied the enantiomer for 1-E.
[b] See footnote a to table 3.
[c] See footnote b to table 3. Their observations were for the β anomer.

6. Experimental Procedures

6.1. Preparation and Purification of the Compounds

The individual compounds listed in table 1 were prepared by the methods given in the references cited. Each compound was recrystallized from an appropriate solvent until further recrystallization caused no change in its melting point or optical rotation.

For the preparation of 6-deoxy-β-L-mannose (compound 12), 11.1 g of compound 11 was dissolved in 200 ml of boiling absolute ethanol under reflux and the solution was evaporated under diminished pressure to a sirup; the material was freed from water by (4 times) dissolving it in 100 ml of absolute ethanol, adding 100 ml of benzene, and evaporating to dryness. The resulting colorless crystals (10 g) were dissolved in 220 ml of boiling acetone under reflux, and the solution was cooled, to give 5.9 g of a crystalline mixture of the α and β anomers of the anhydrous sugar, mp 114–116°. (Jackson and Hudson had supposed this material to be a compound.) The dry, finely powdered mixture was shaken with absolute ethanol (4 vols.) for 5 min at room temperature, the suspension was filtered with suction (rubber dam), the crystals were immediately re-extracted in the same way with the same volume of absolute ethanol, and the crystals were rapidly removed by suction filtration (rubber dam) and dried in a vacuum desiccator (Desiguard) over phosphorus pentaoxide at 0.1 mm; the crystals had mp 127–129°.

6.2. Preparation of the Equilibrium Mixtures

The crystalline compound (0.5 g) was weighed into a 25-ml volumetric flask, water was added, the solution was made to 25 ml with water, and the specific rotation was observed periodically until mutarotation was complete. For sugars displaying no mutarotation, the solution was kept overnight at room temperature. A portion (0.1 ml) was now transferred, by pipet, to a 5-ml flask containing 500 mg of potassium chloride. The pipet and the neck of the 5-ml flask were washed with water, and the washings were added to the flask contents, which were then brought to about 3 ml with water. The solution was frozen and lyophilized, giving a dry mass containing 0.4 mg (or its equivalent) of the sugar or sugar compound per 100 mg of potassium chloride.

For 2,7-anhydro-β-D-*altro*-heptulose (sedoheptulosan) monohydrate (compound 24), 0.25 g was dis-

solved in 20 ml of 1 percent aqueous hydrochloric acid, and the solution was heated, under reflux, in a boiling-water bath for 1 hr. The solution was de-ionized by passage through columns of (a) Duolite A–4(OH^-)(20 ml) and (b) a mixture of 2 ml of this resin with 2 ml of Amberlite IR–120 (H^+), with elution with water until the total volume of final effluent was 125 ml. One milliliter of this neutral effluent was added to 500 mg of potassium chloride in a 5-ml flask, 2 ml of water was added, and the solution was frozen and lyophilized, giving a dry mass containing the equivalent of 0.4 mg of compound 24 per 100 mg of potassium chloride. It should be noted that heating of a 0.07 *M* solution of sedoheptulosan monohydrate in 0.2 *N* hydrochloric acid for 1 hr at 100° affords [14] a mixture of 80.4 percent of sedoheptulosan monohydrate with 3.4 percent of 2,7-anhydro-β-D-*altro*-heptulofuranose, 14.8 percent of D-*altro*-heptulose, and 1.4 percent of 5-(1,2-dihydroxyethyl)-2-furaldehyde.

6.3. Preparation of the Pellets

For spectrophotometric study, samples of the individual compounds were prepared as pellets consisting of the crystalline compound suspended in an alkali-metal halide, exactly as previously described [15]. For the range of 5000 to 667 cm^{-1}, a concentration of 0.4 mg of the compound per 100 mg of potassium chloride was used. The spectrum of compound 20 in this range was also recorded at the same concentration in potassium iodide. For the range of 667 to 250 cm^{-1}, the following weights of compound per 100 mg of potassium iodide were used—compound 25 : 1 mg; compounds 5 and 17 : 1.34 mg; compounds 2 to 4 and 7 : 3 mg; and for the rest of the compounds: 2 mg. In this range, the spectrograms for compounds 16 and 18 in Nujol were recorded at several concentrations.

For the lyophilized, equilibrium mixtures, the dry lyophilizate (already containing the desired proportion of potassium chloride) was pressed directly into a pellet.

6.4. Measurement of Infrared Absorption

The spectrograms are shown in figures 1 and 2. Those in figure 1 for compound 20 and its equilibrium mixture (20–E) were recorded with a Beckman Model IR4 (double-beam) spectrophotometer equipped with prisms of sodium chloride. The others were recorded with a Perkin-Elmer Model 21 (double-beam) spectrophotometer equipped with a prism of sodium chloride (for the range of 5000 to 667 cm^{-1}) and of cesium bromide (for the range of 667 to 250 cm^{-1}), as previously described [15].

Some absorption attributable to water (in the compound, the alkali halide, or both) was observed at 1639 cm^{-1} and, attributable to atmospheric water vapor, in the far-infrared curves. These regions are drawn on the spectrograms with dashed lines which are not to be interpreted quantitatively.

6.5. Spectra Measured Under Different Conditions

Because of the possibility of interaction of the various sugars with the pelleting halide under high pressure (previously observed [16] for 8 out of 24 aldopyranosides), the spectra of the sugars were also recorded in a Nujol mull in the range of 667 to 250 cm^{-1}. For 16 of the 27 sugars, the spectra obtained with either medium matched well; for 5, the spectra in potassium iodide were not well defined, but matched those in Nujol (compounds 8, 9, 15, 16, and 26). However, the following compounds gave spectrograms that were *different* in Nujol and in potassium iodide: compounds 3, 14, 20, 24, 25, and 27.

In view of these observations, the spectra obtained with a Nujol mull were used exclusively for measuring the positions of absorption bands in the range of 667 to 250 cm^{-1}, not only for the sugars that gave unsatisfactory spectra in potassium iodide, but also (in order to keep the measurements strictly comparable) for the other sugars.

Farmer [6] had noted that, in the range of 5000 to 667 cm^{-1}, "α-glucopyranose" gave a spectrum in potassium iodide that differed from that in potassium bromide. We therefore recorded the spectra of compound 20 (a sugar that gave a poor spectrum in potassium iodide in the range of 667 to 250 cm^{-1}) in potassium iodide and in potassium chloride, at identical concentration in pellets of the same weight, for the range of 5000 to 667 cm^{-1}; the spectrum in potassium iodide was less detailed than that in potassium chloride.

The authors express their gratitude to J. D. Moyer for preparing and lyophilizing the equilibrated solutions. They also thank J. E. Stewart, J. J. Comeford, and F. P. Czech for recording the infrared absorption spectra.

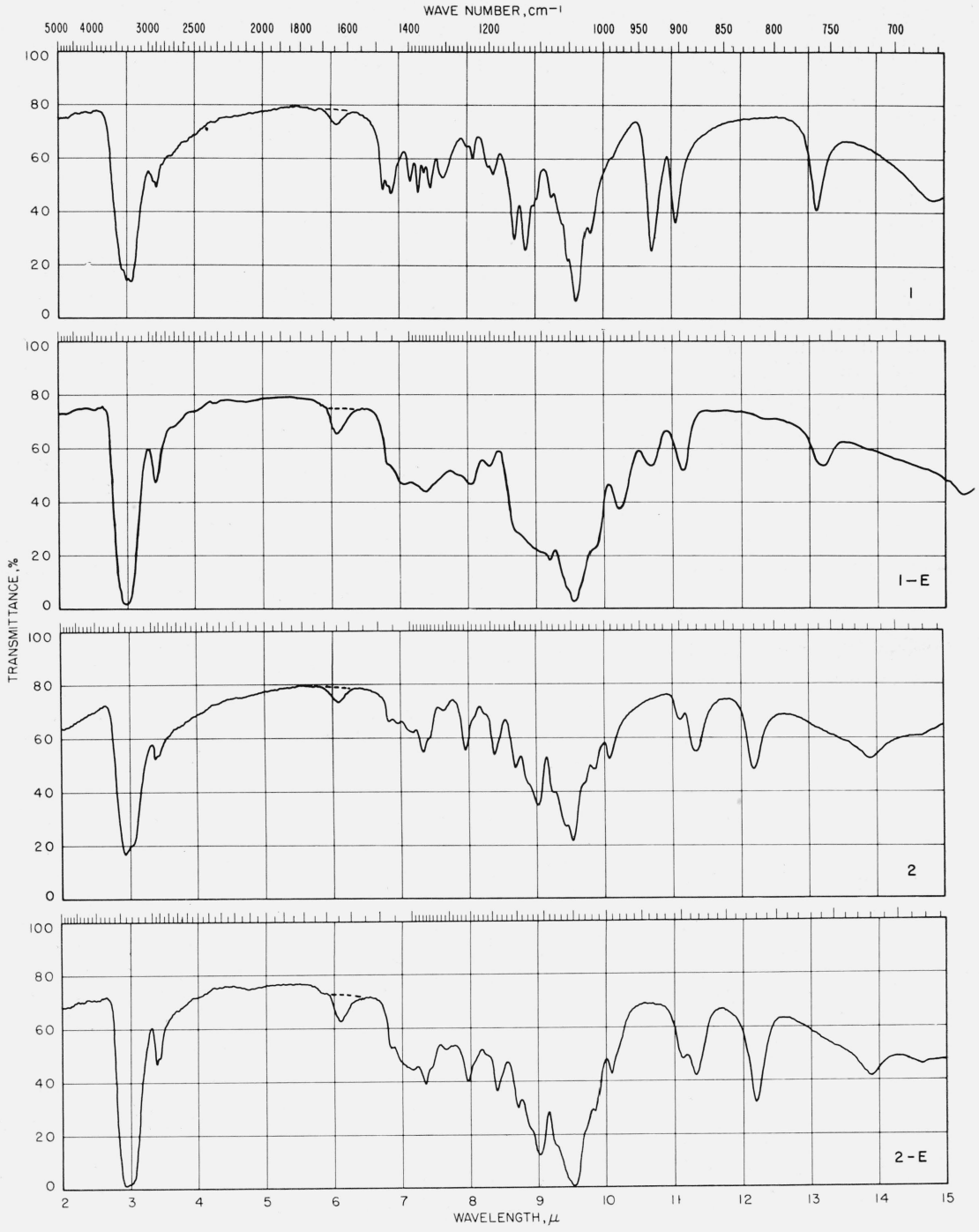

FIGURE 1. *Spectrograms of materials in potassium chloride pellets.*

1, *α*-D-Xylose; **1-E,** D-xylose (equilibrium); **2,** (?)-L-*xylo*-hexulose; **2-E,** L-*xylo*-hexulose (equil.).

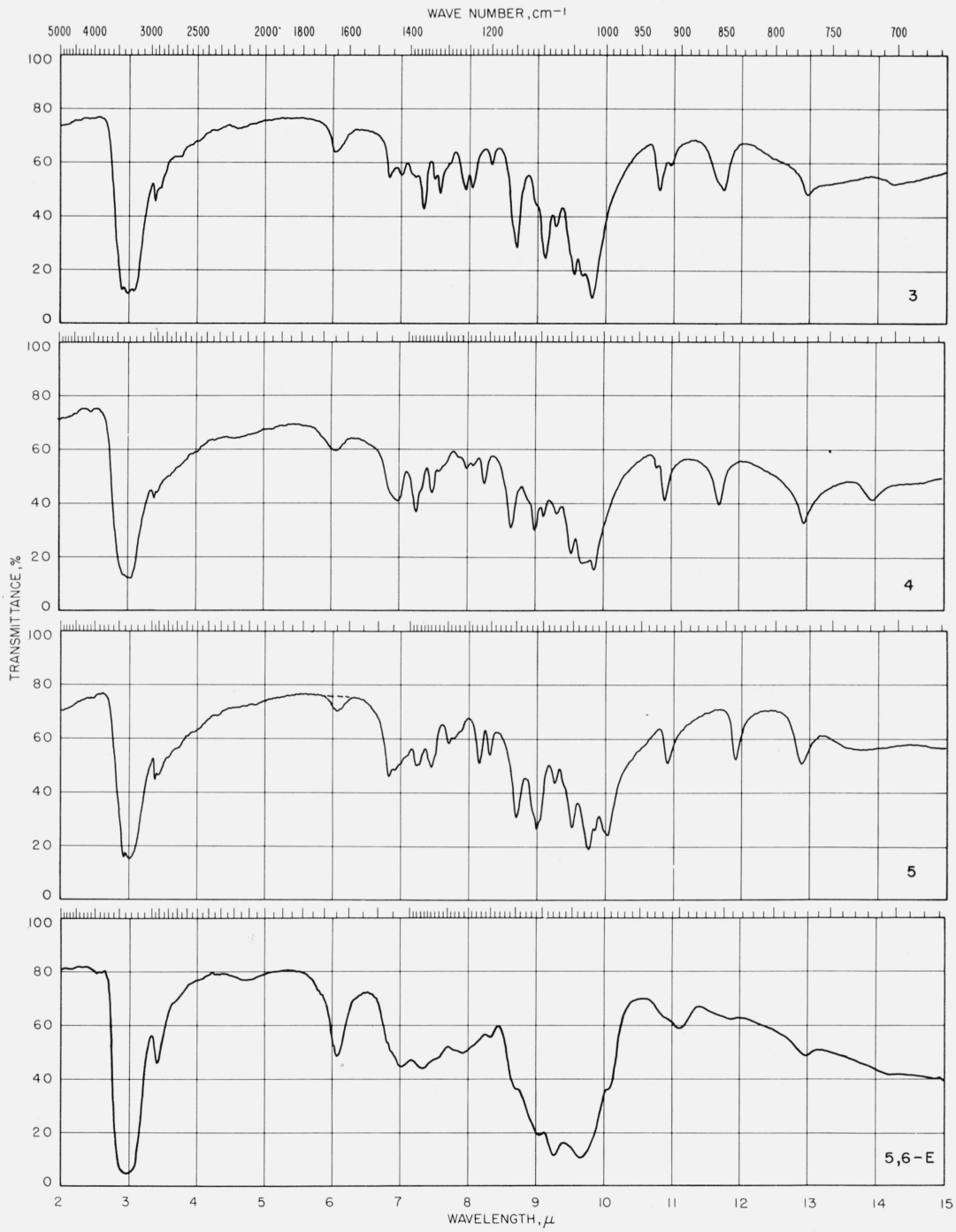

FIGURE 1. *Spectrograms of materials in potassium chloride pellets.*—Continued

3, α-D-glucose·0.5 NaCl·0.5 H_2O; **4,** α-D-glucose monohydrate; **5,** α-D-glucose; **5, 6–E,** D-glucose (equil.).

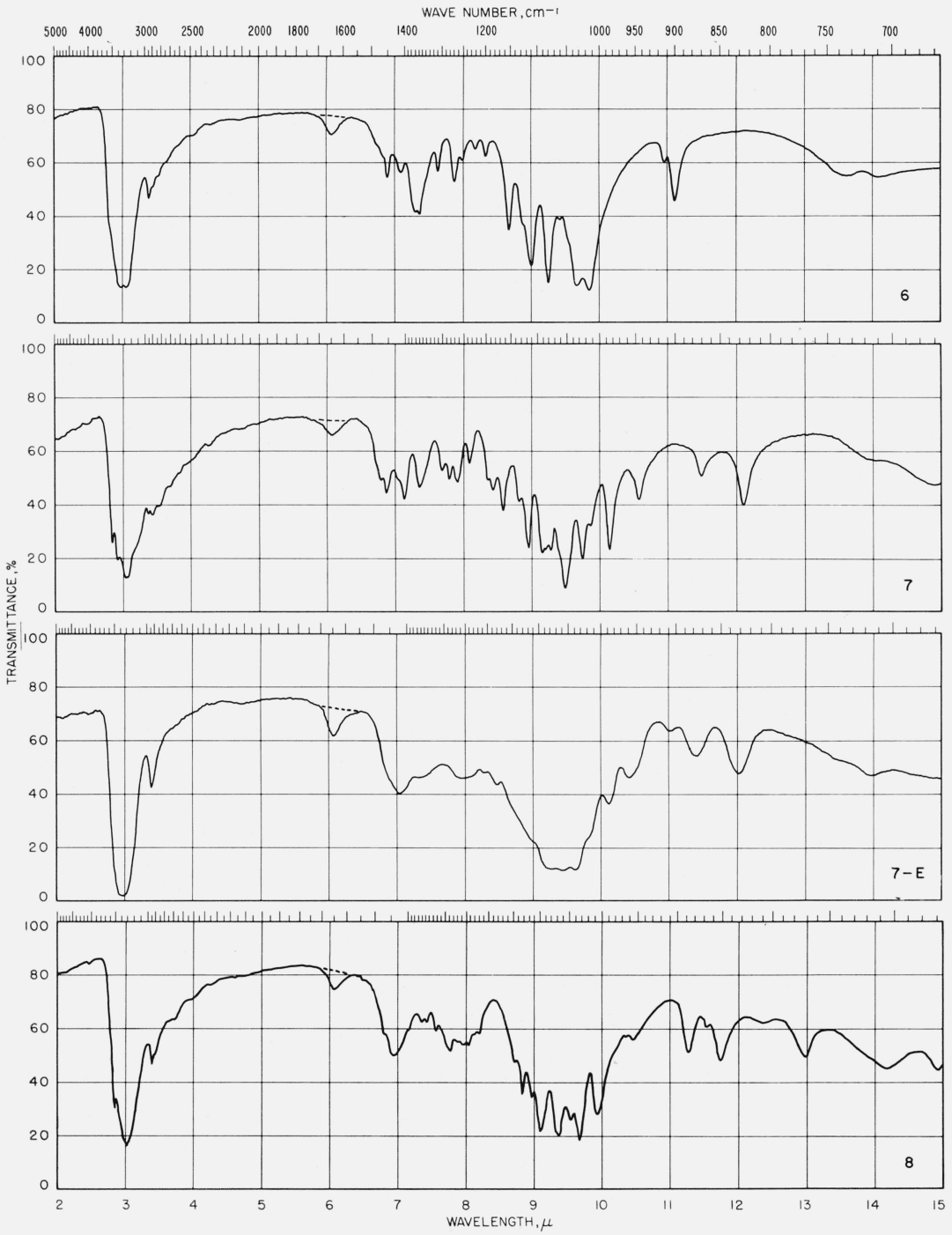

FIGURE 1. *Spectrograms of materials in potassium chloride pellets.*—Continued

6, β-D-glucose; **7,** α(?)-D-*gluco*-heptulose; **7-E,** D-*gluco*-heptulose (equil.); **8,** α-D-lyxose.

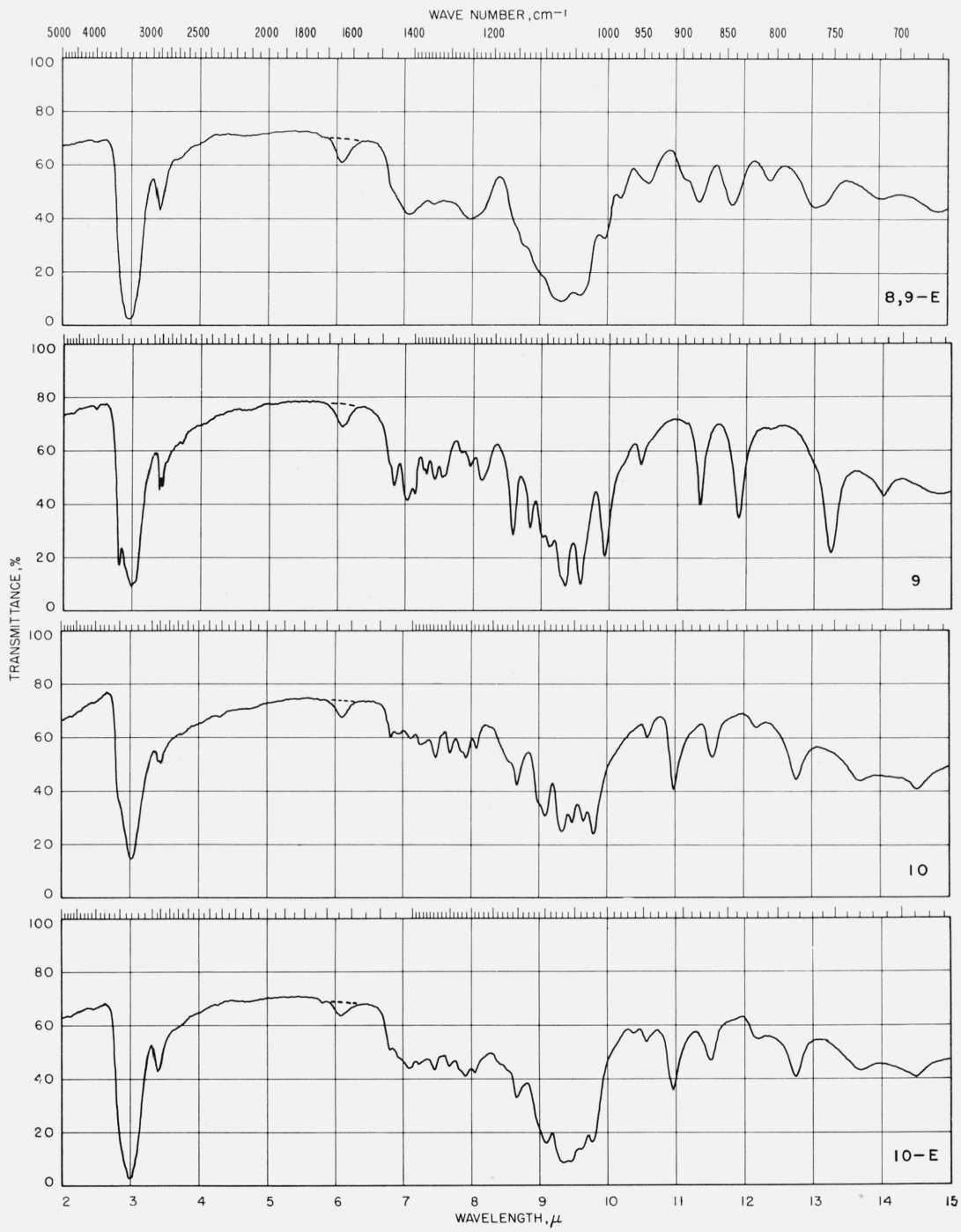

FIGURE 1. *Spectrograms of materials in potassium chloride pellets.*—Continued

8,9–E, D-lyxose (equil.); **9,** *β*-D-lyxose; **10,** (?)-D-*lyxo*-hexulose; **10–E,** D-*lyxo*-hexulose (equil.).

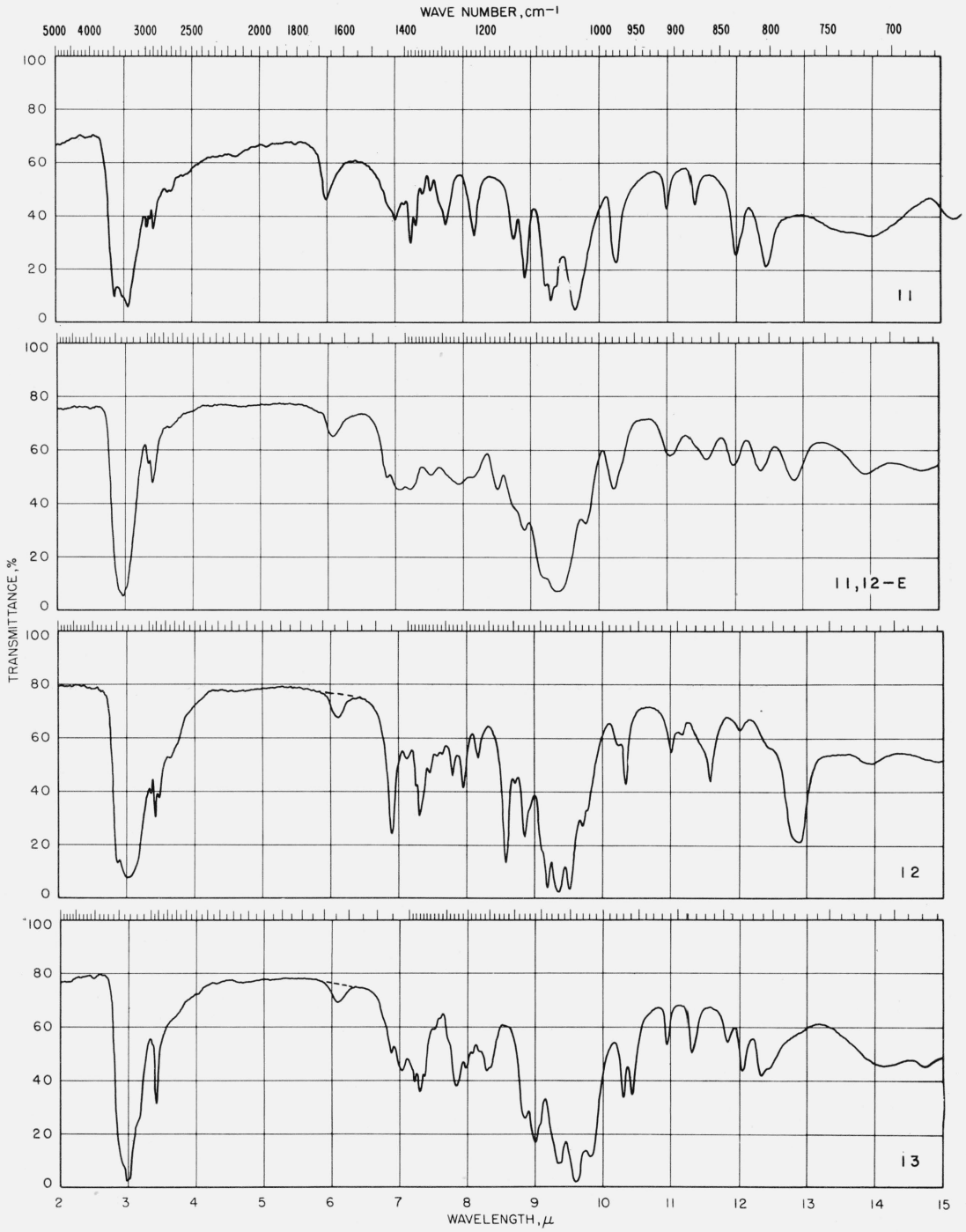

FIGURE 1. *Spectrograms of materials in potassium chloride pellets.*—Continued

11, 6-deoxy-α-L-mannose monohydrate; **11, 12-E,** 6-deoxy-L-mannose (equil.); **12,** 6-deoxy-β-L-mannose; **13,** α-D-mannose.

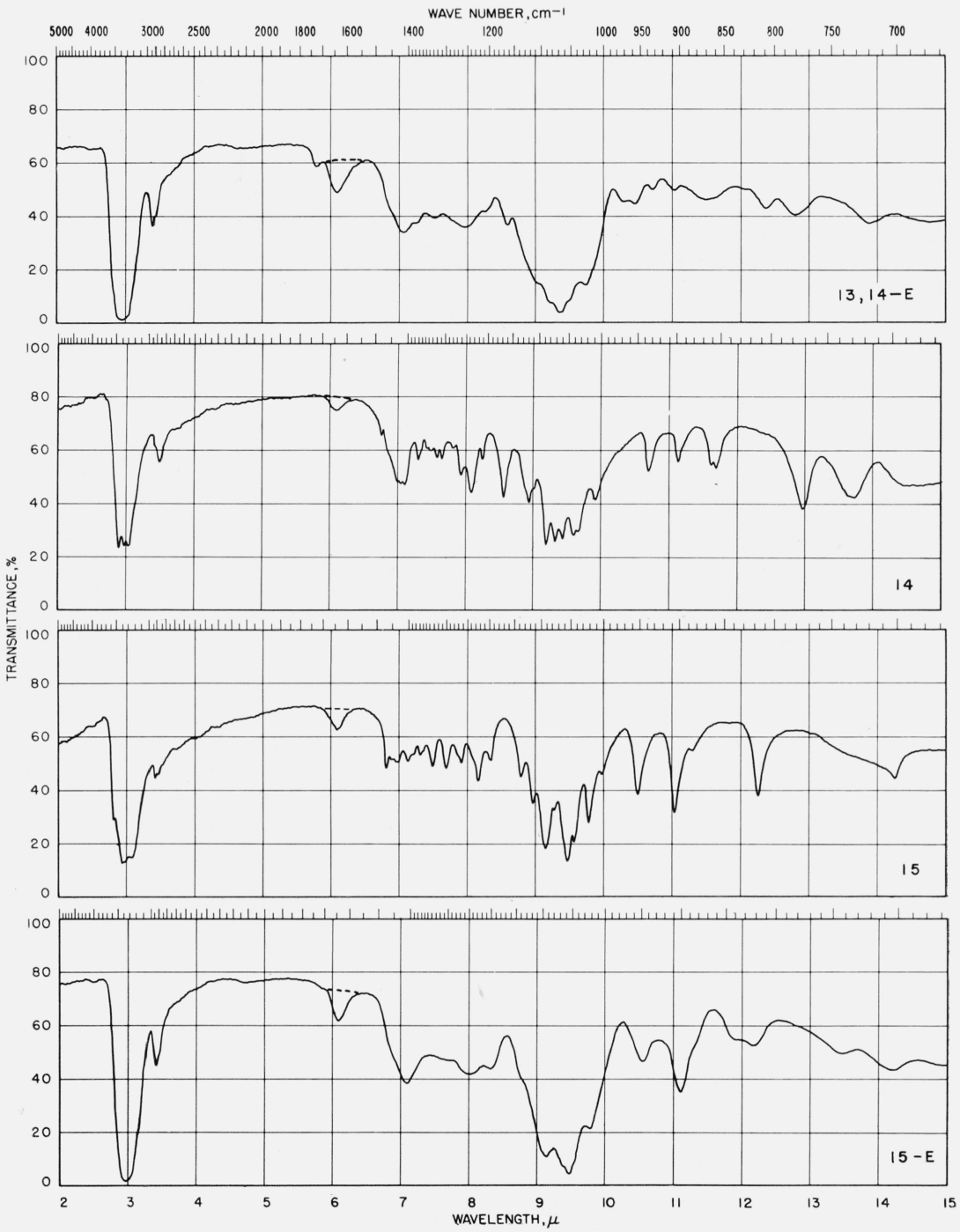

FIGURE 1. *Spectrograms of materials in potassium chloride pellets.*—Continued

13, 14-E, D-mannose (equil.); **14,** β-D-mannose; **15,** (?)-D-*manno*-heptulose; **15-E,** D-*manno*-heptulose (equil.).

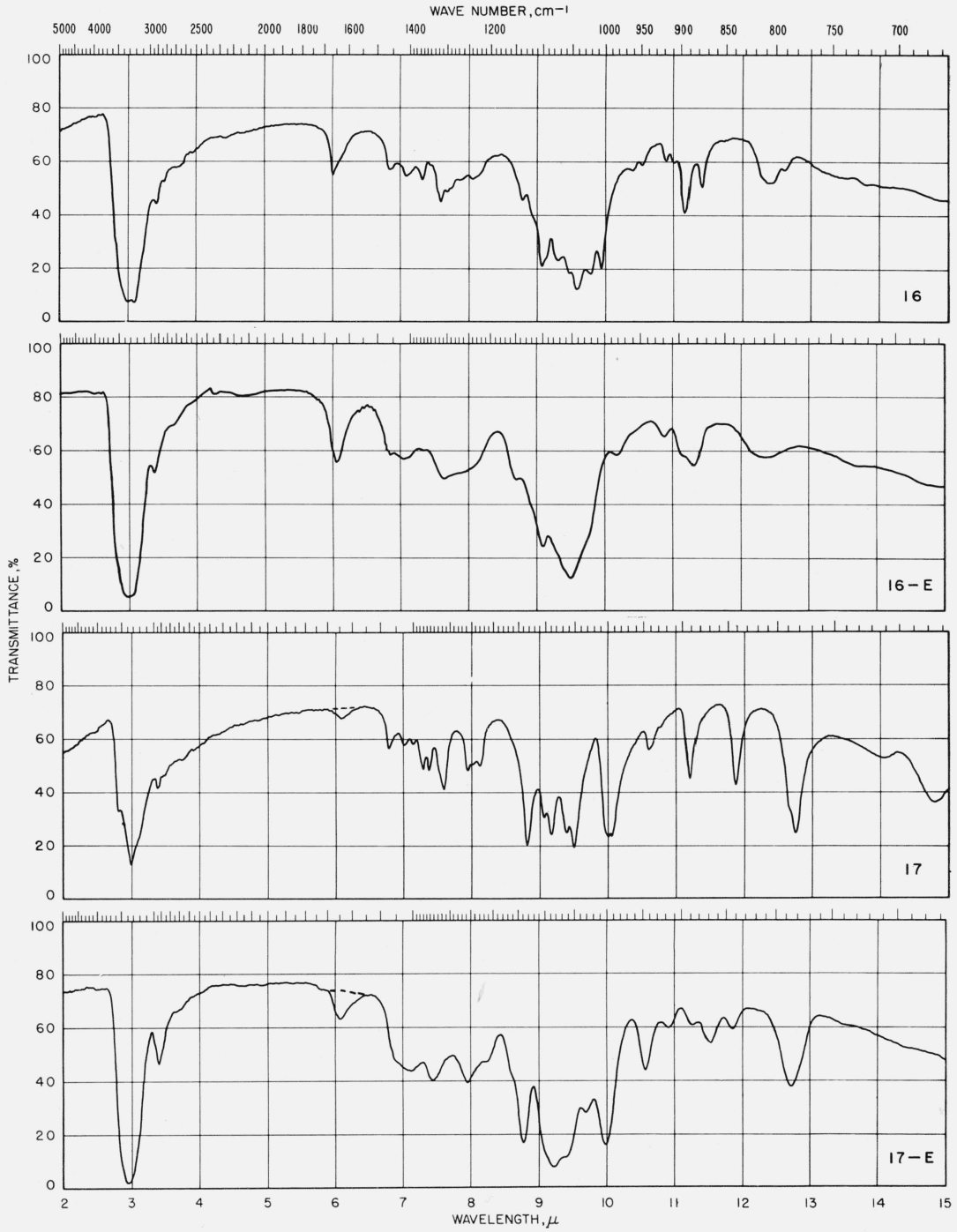

FIGURE 1. *Spectrograms of materials in potassium chloride pellets.*—Continued

16, (?)-D-gulose·0.5 $CaCl_2$·0.5 H_2O; **16–E,** D-gulose·0.5 $CaCl_2$ (equil.); **17,** β-D-arabinose; **17–E,** D-arabinose (equil.).

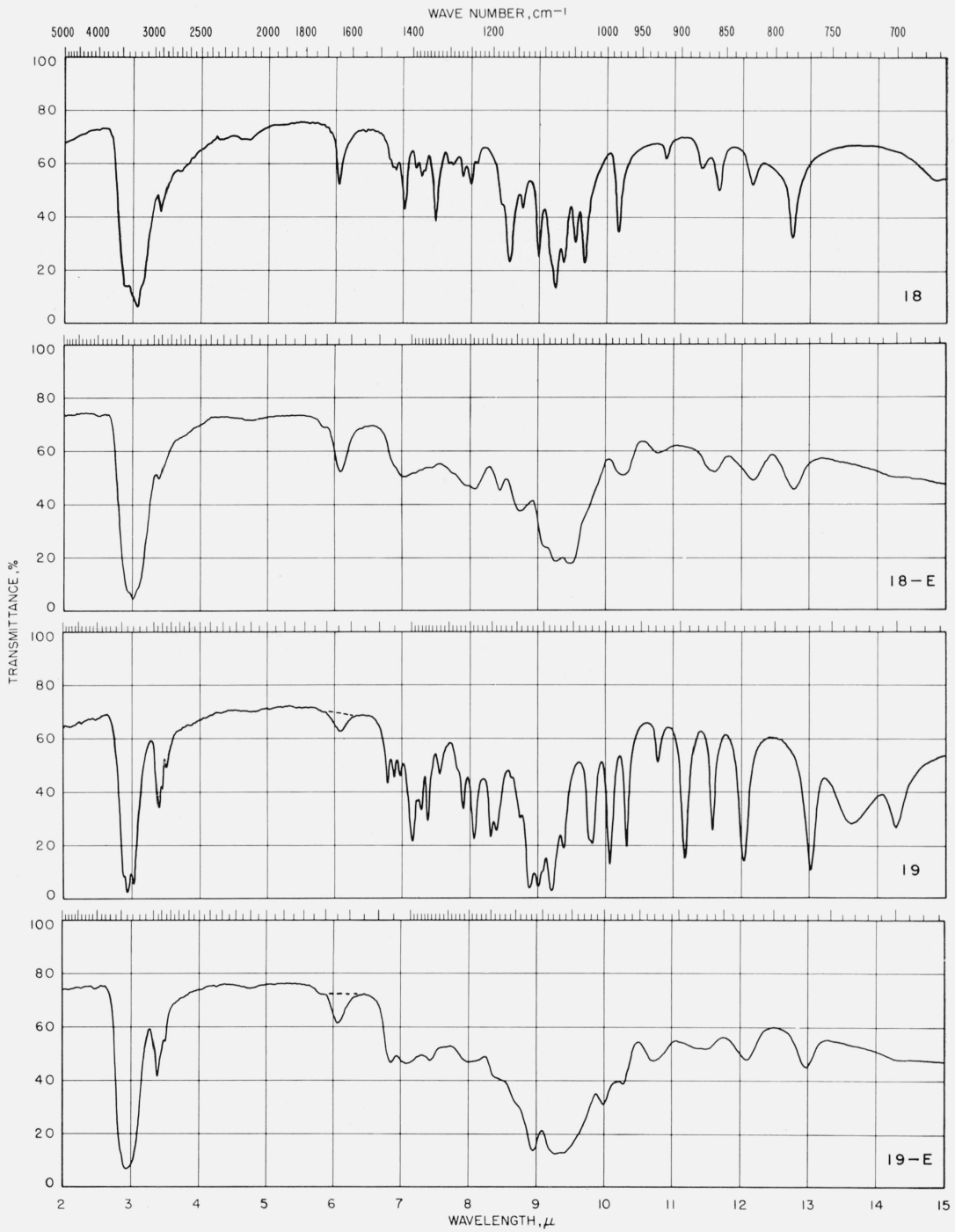

FIGURE 1. *Spectrograms of materials in potassium chloride pellets.*—Continued

18, (?)-D-*arabino*-hexulose·0.5 $CaCl_2$·1.5 H_2O; **18-E,** D-*arabino*-hexulose·0.5 $CaCl_2$ (equil.); **19** 3-*O*-methyl-(?)-D-*arabino*-hexulose; **19-E,** 3-*O*-methyl-D-*arabino*-hexulose (equil.).

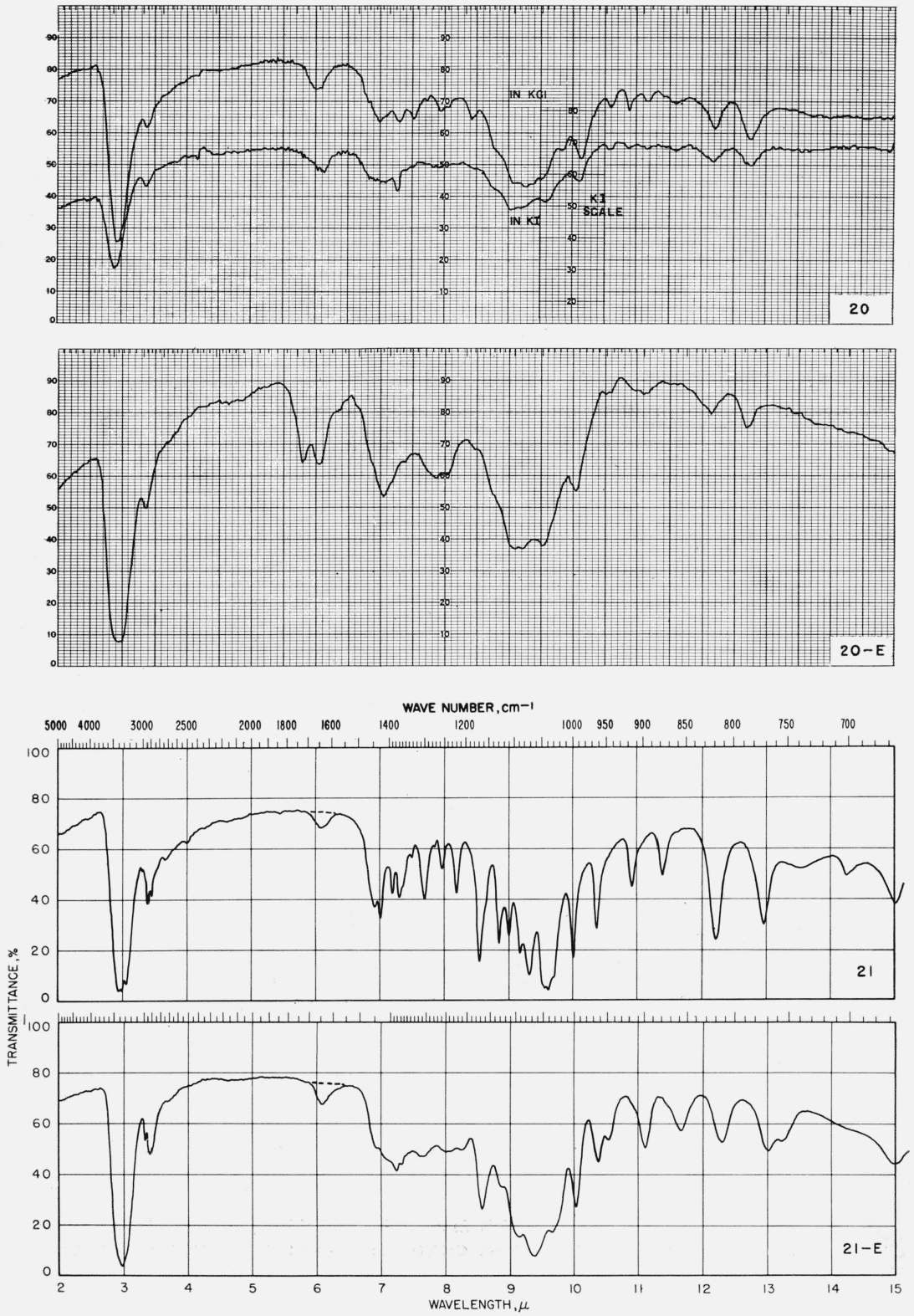

FIGURE 1. *Spectrograms of materials in potassium chloride pellets.*—Continued

20, β-D-*manno*-3-heptulose monohydrate; **20–E,** D-*manno*-3-heptulose (equil.); **21,** 6-deoxy-α-L-galactose; **21–E,** 6-deoxy-L-galactose (equil.).

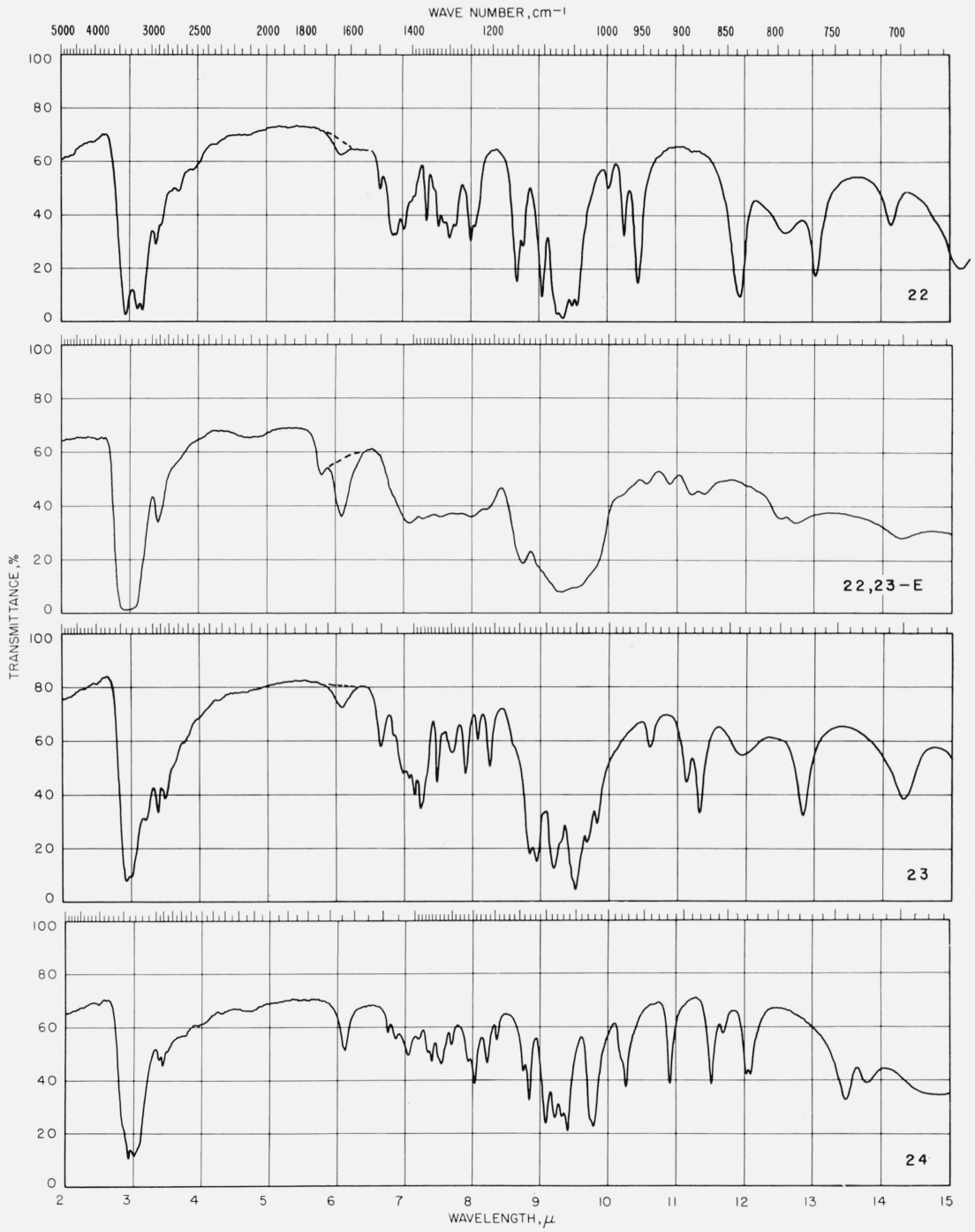

FIGURE 1. *Spectrograms of materials in potassium chloride pellets.*—Continued

22, α-D-galactose; **22,23-E,** D-galactose (equil.); **23,** β-D-galactose; **24,** 2,7- anhydro-β-D-*altro*-heptulose monohydrate.

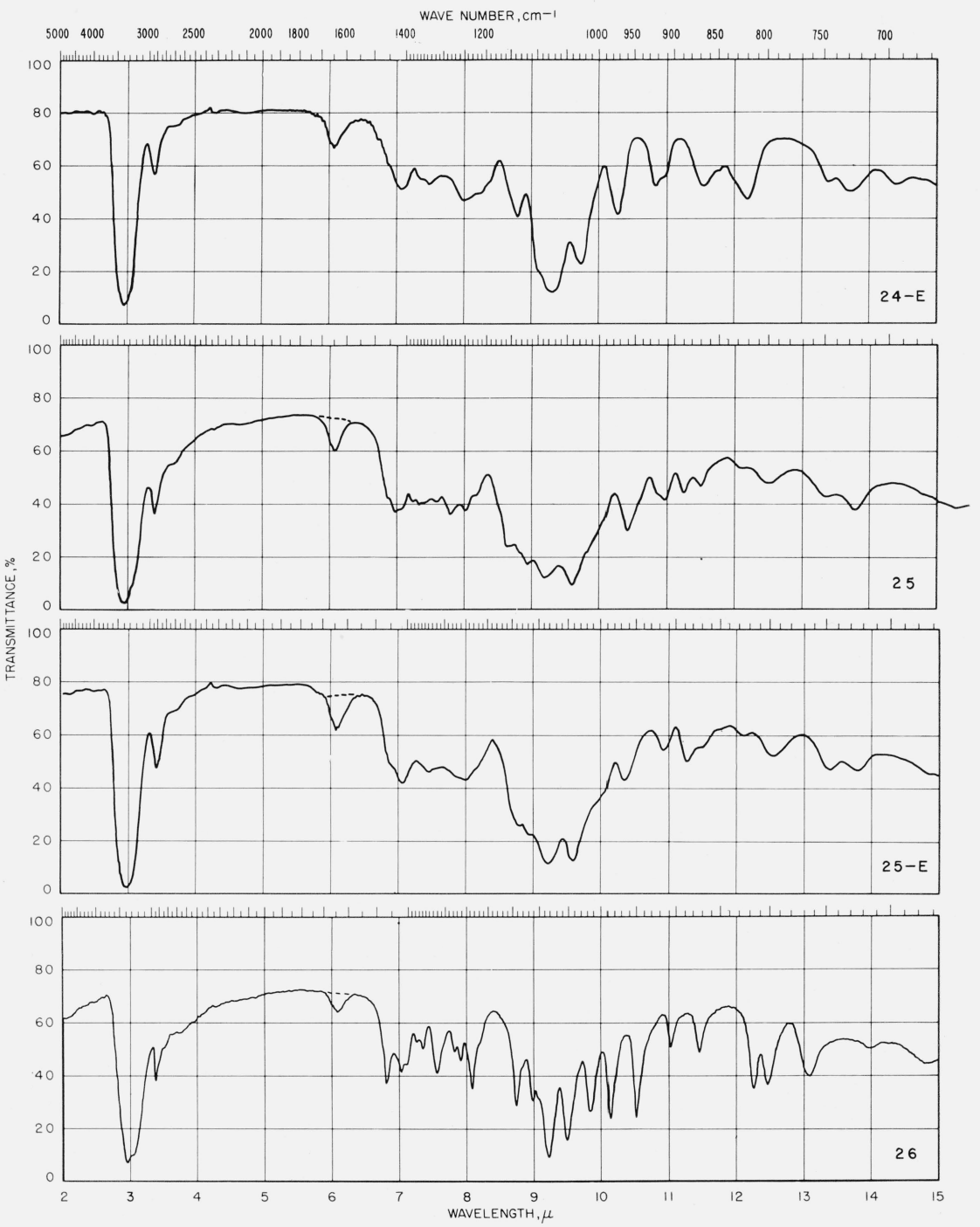

FIGURE 1. *Spectrograms of materials in potassium chloride pellets.*—Continued

24–E, mixture from treatment of compound 24 with 1 percent hydrochloric acid; **25,** β(?)-D-ribose; **25–E,** D-ribose (equil.); **26,** α-D-talose.

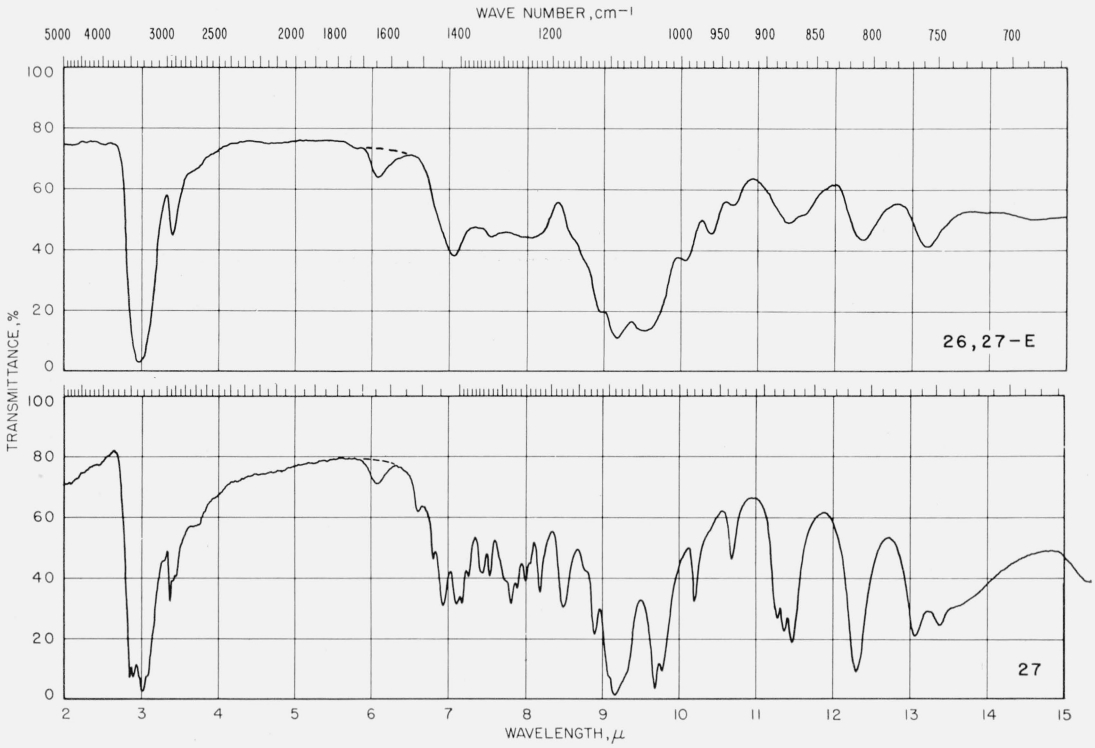

FIGURE 1. *Spectograms of materials in potassium chloride pellets.*—Continued

26, 27–E, D-talose (equil.); **27,** β-D-talose.

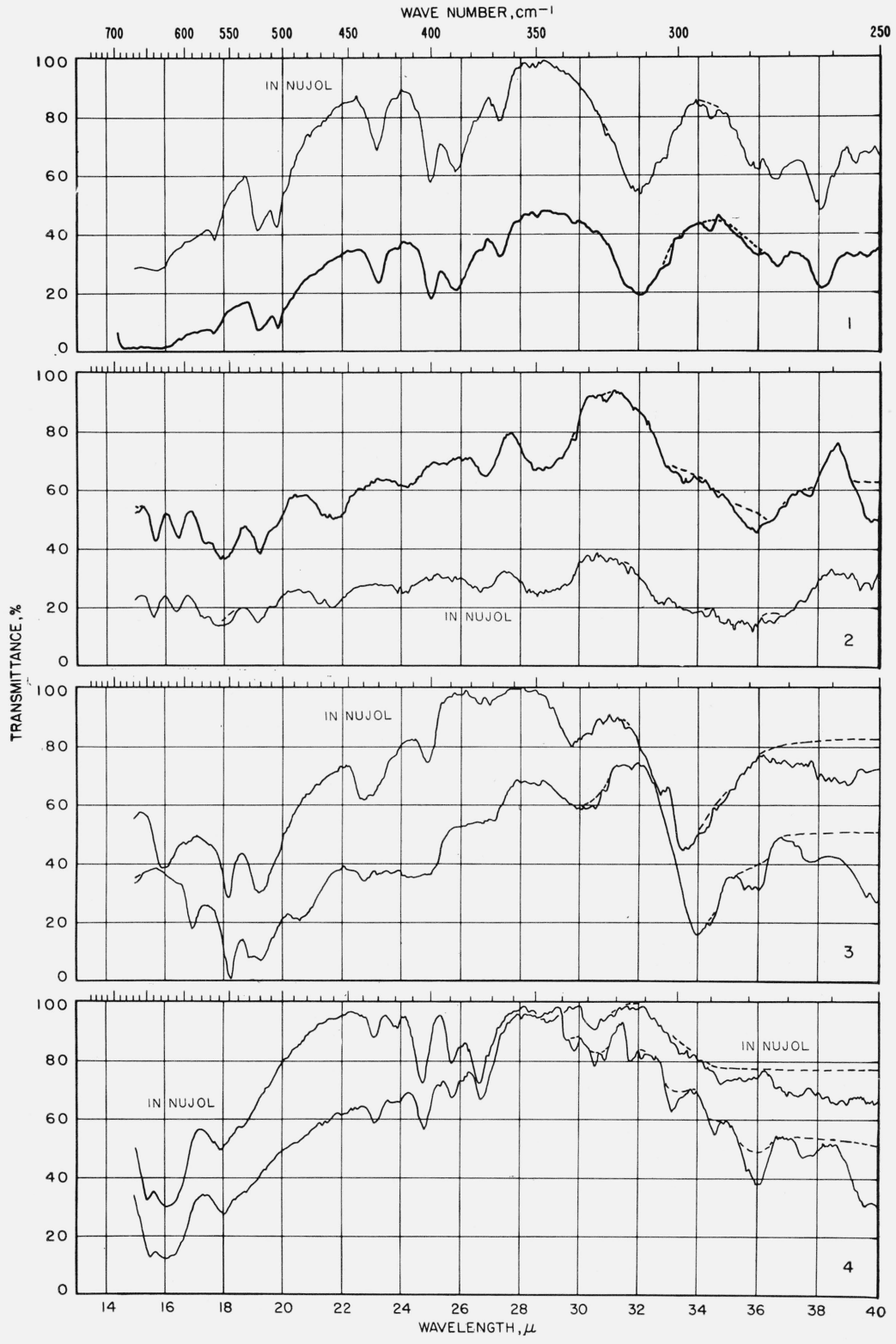

FIGURE 2. *Spectrograms of materials in Nujol mulls and in potassium iodide pellets.*

1, α-D-Xylose; **2,** (?)-L-*xylo*-hexulose; **3,** α-D-glucose·0.5 NaCl·0.5 H_2O; **4,** α-D-glucose monohydrate.

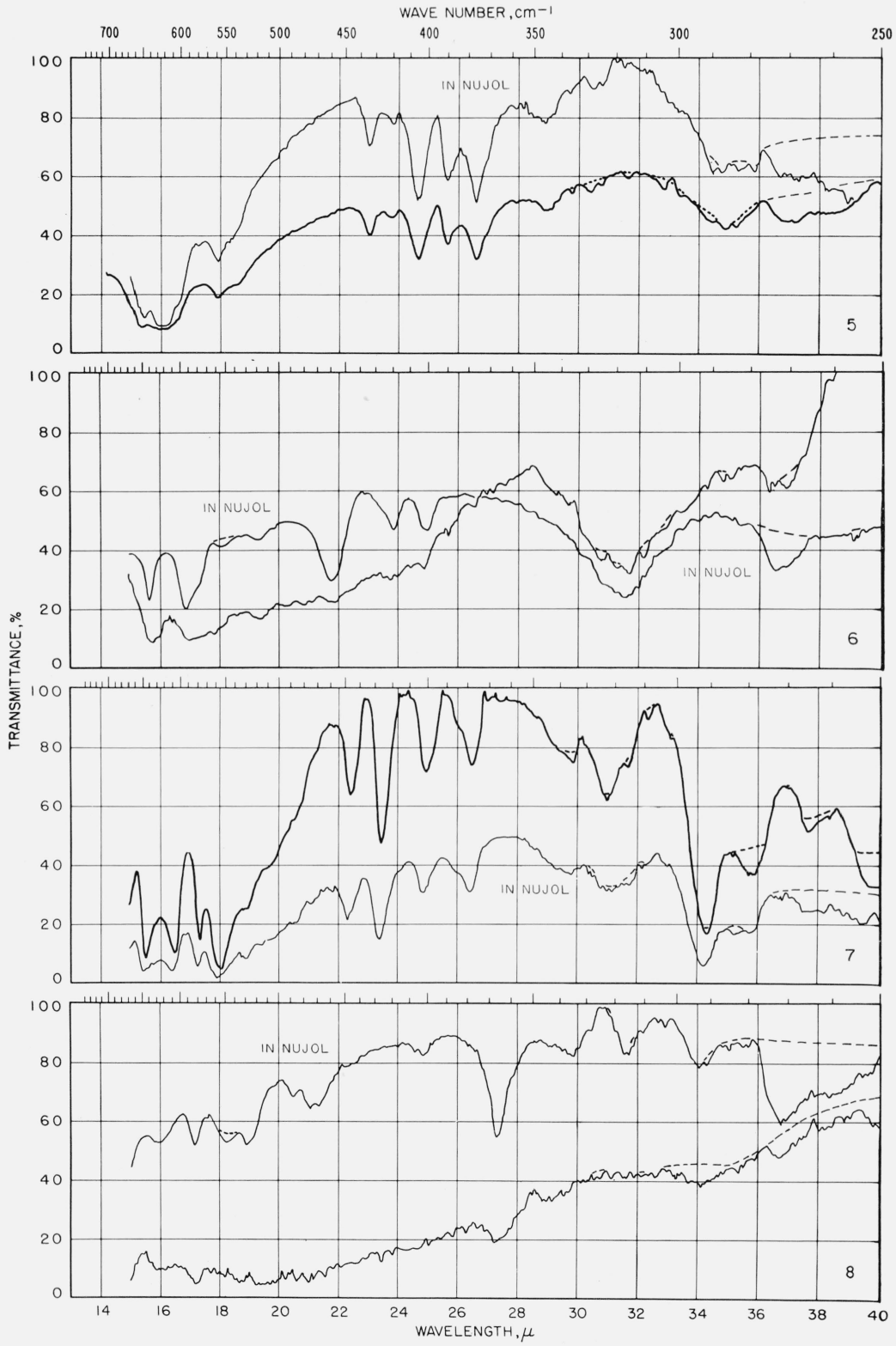

FIGURE 2. *Spectrograms of materials in Nujol mulls and in potassium iodide pellets.*—Continued

5, α-D-glucose; **6**, β-D-glucose; **7**, α(?)-D-*gluco*-heptulose; **8**, α-D-lyxose.

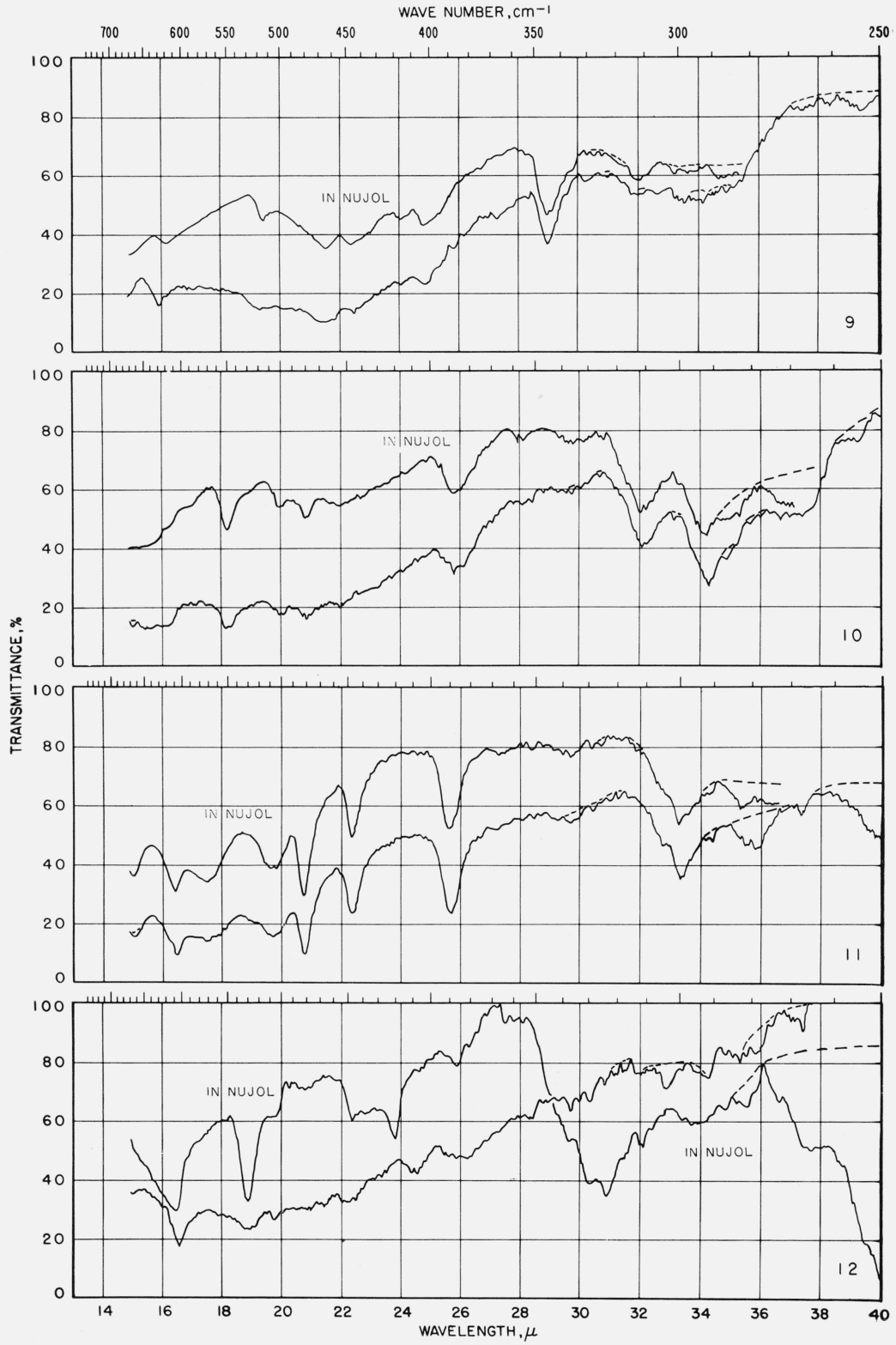

FIGURE 2. *Spectrograms of materials in Nujol mulls and in potassium iodide pellets.*—Continued

9, β-D-lyxose; **10,** (?)-D-*lyxo*-hexulose; **11,** 6-deoxy-α-L-mannose monohydrate; **12,** 6-deoxy-β-L-mannose.

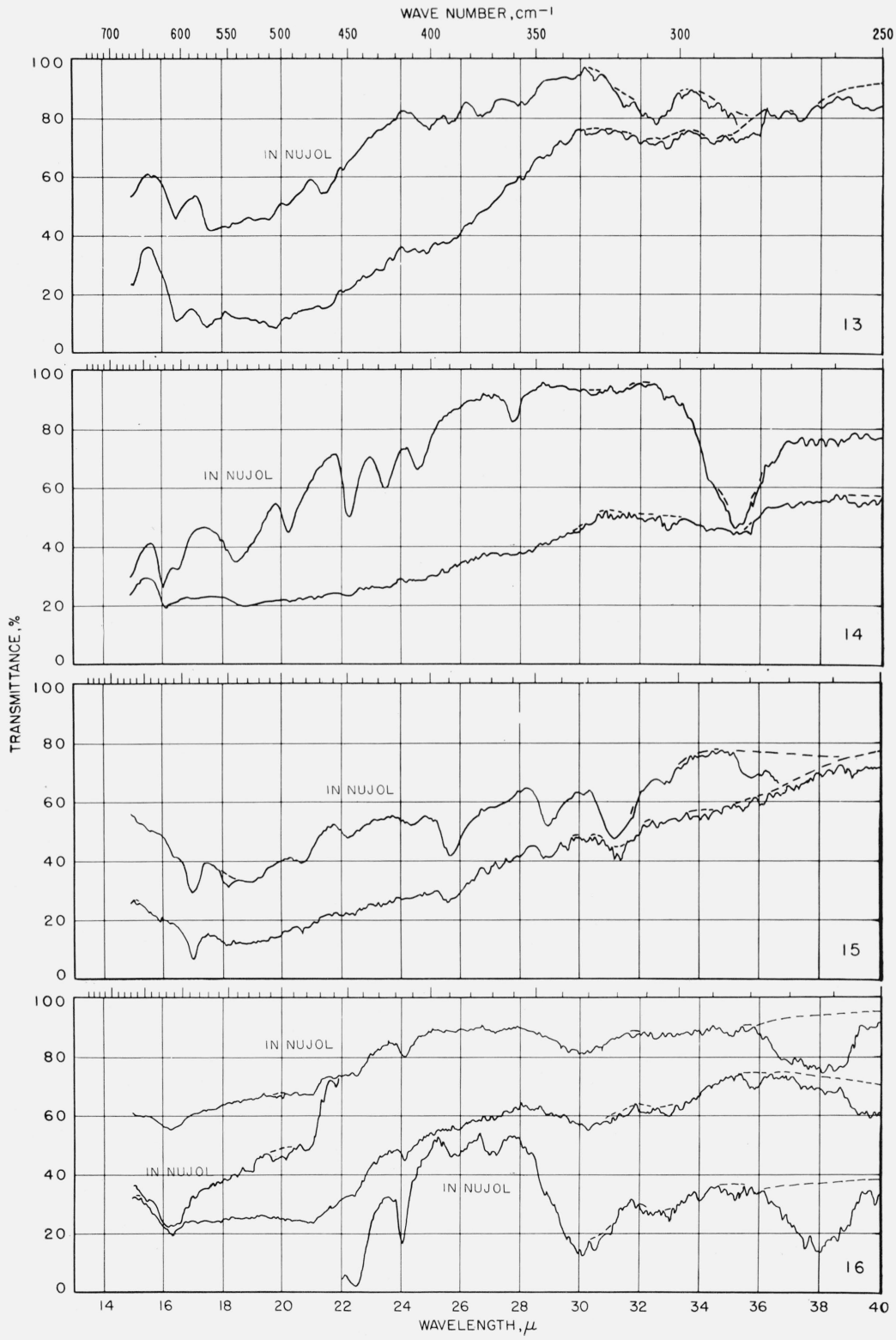

FIGURE 2. *Spectrograms of materials in Nujol mulls and in potassium iodide pellets.*—Continued

13, α-D-mannose; **14,** β-D-mannose; **15,** (?)-D-*manno*-heptulose; **16,** (?)-D-gulose·0.5 $CaCl_2$·0.5 H_2O.

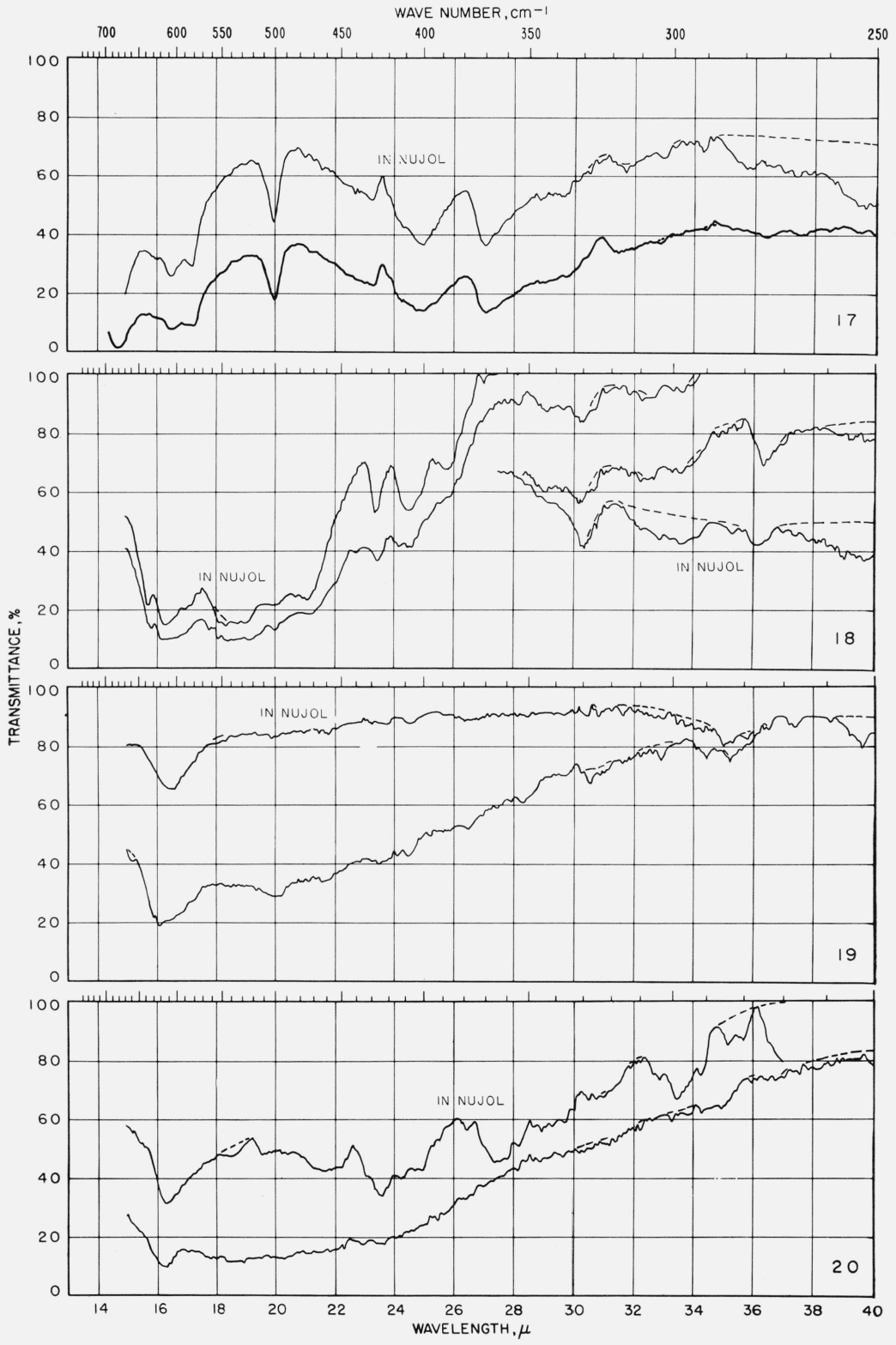

FIGURE 2. *Spectrograms of materials in Nujol mulls and in potassium iodide pellets.*—Continued

17, β-D-arabinose; **18,** (?)-D-*arabino*-hexulose·0.5 $CaCl_2$·1.5 H_2O; **19,** 3-*O*-methyl-(?)-D-*arabino*-hexulose; **20,** β-D-*manno*-3-heptulose monohydrate.

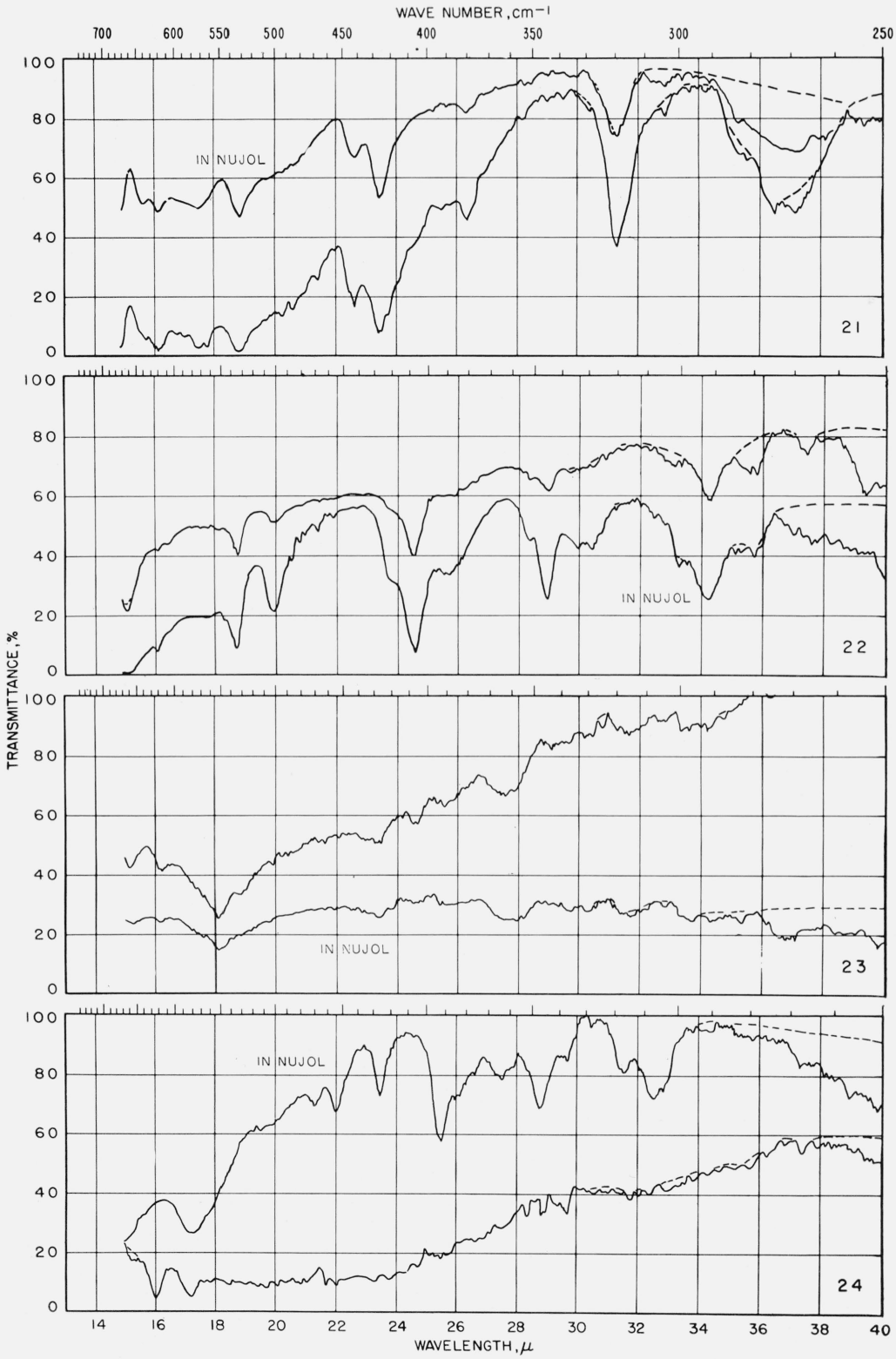

FIGURE 2. *Spectrograms of materials in Nujol mulls and in potassium iodide pellets.*—Continued

21, 6-deoxy-α-L-galactose; **22,** α-D-galactose; **23,** β-D-galactose; **24,** 2,7-anhydro-β-D-*altro*-heptulose monohydrate.

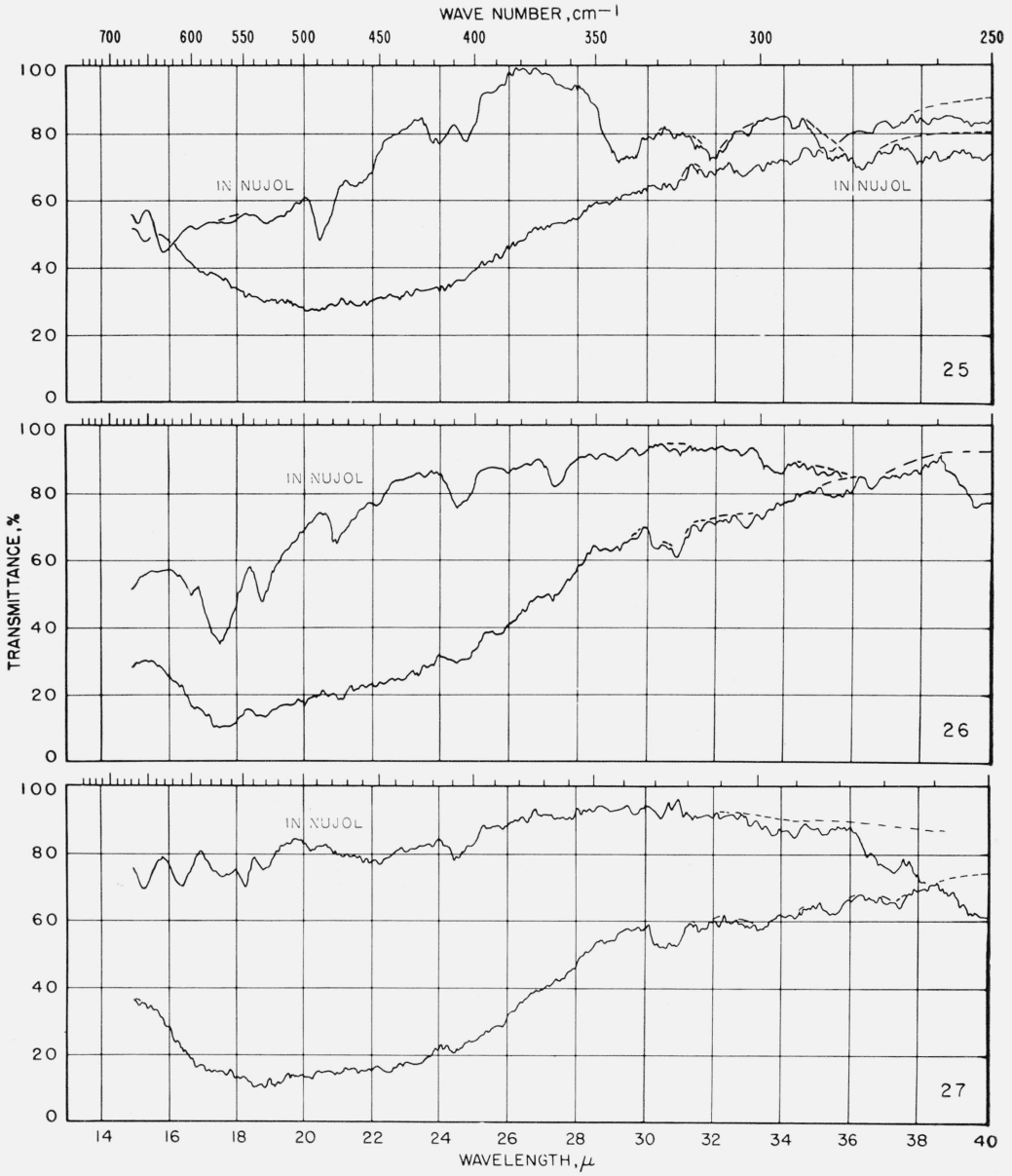

FIGURE 2. *Spectrograms of materials in Nujol mulls and in potassium iodide pellets.*—Continued

25, β(?)-D-ribose; **26**, α-D-talose; **27**, β-D-talose.

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